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THE
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AND
JOURNAL OF PHYSICAL SCIENCE.

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IN ALL ITS APPLICATIONS TO

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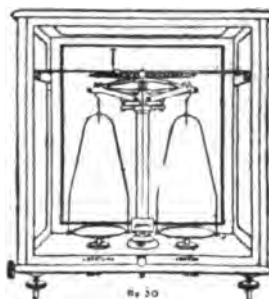
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No. 2380.—JULY 7, 1905.

THORIA, THE ESTIMATION AND SEPARATION OF FROM THE YTTRIUM-CERIUM GROUP OF OXIDES.

By W. B. GILES, F.I.C.

ON reviewing the various methods of separation that have been proposed by different chemists for the separation of thoria from the other members of this group of earth metals it will be found that all of them in practice leave something to be desired. In some of these methods the separations are imperfect, and have to be repeated many times. To this class belongs the method depending upon the solubility of thorium oxalate in ammonium oxalate, with subsequent precipitations with sodium thiosulphate. Take, for instance, the method published by Fresenius and Hintz for ascertaining the purity of commercial thorium nitrate (Truchot, "Les Terres Rares," pp. 304—305). They direct 20 grms. of the nitrate to be dissolved in 3 litres of water; this solution is then to be precipitated by sodium thiosulphate, the precipitate re-dissolved in hydrochloric acid, and this operation repeated five times over. It also involves two fusions with potassium bisulphate, eight resolutions in hydrochloric acid, two resolutions in nitric acid, five precipitations with ammonia, two with sodium hypochlorite, and one with oxalic acid, yielding finally 0.0186 of ceric oxide (impure)! Other methods employ reagents difficult to prepare, such as potassium nitride (Dennis), and in another class, organic substances, such as aniline (Kolb); fumaric acid and metanitrobenzoic acid (Metzner) have been proposed. The introduction of organic matters with a high percentage of carbon and the use of alcohol is undesirable if it can be avoided. In making analyses of minerals containing the rare earths, the author experienced difficulties in accurately separating thoria from the other allied bodies, and he sought for a method of effecting this which should embrace the following advantages. It should be simple and at the same time effective, *i.e.*, it should not require more than one or at most two repetitions for an absolute separation. Finally, it should introduce nothing into the solution which cannot be easily removed, thus facilitating the after estimation of the other constituents. After a course of experiments with a large number of reagents he found that in pure lead carbonate we have a very valuable reagent for the estimation and separation of thoria and some other bodies (zirconia, ceric oxide, and ferric oxide) from the cerium-yttrium group of earths. If we take a solution of these bodies in the form of nitrates, either neutral or slightly acidified with nitric acid, and stir in an excess of pure moist precipitated carbonate of lead, the following results are obtained:—

Wholly Precipitated—

Thoria.
Zirconia.
Ceric oxide.
(Ferric oxide).

Slowly and Imperfectly Precipitated—

Uranic oxide.
Chromium sesquioxide.
(Alumina).

Not Precipitated—

Cerous oxide.
Lanthana.
Neodymia.
Praseodymia.
Yttria.
Samarita.

And the yttria group generally as far as has been noticed.*

In carrying out these experiments, if correct results are desired, it is absolutely essential to have the carbonate of lead *pure*, as in the course of the author's preliminary experiments he met with some anomalous results which were ultimately traced to impurities in the (so-called C. P.) lead carbonate employed). These impurities consist of alkaline carbonates, basic acetates, and nitrates, and almost invariably some ferric oxide. Lead carbonate retains traces of fixed alkaline carbonates with great tenacity (as is the case with calcium, barium, and strontium carbonates), and these cannot be removed entirely with any reasonable amount of washing. Therefore, even at the risk of appearing somewhat tedious, it is well to describe how a pure and suitable lead carbonate is obtained.

"Re-crystallised pure lead nitrate" is dissolved in about five times its own weight of water, warmed to about 70° C., and then sufficient solution of re-sublimed ammonium sesquicarbonate is added to cause a decided precipitation; the whole is kept well agitated, and from time to time a little of the turbid fluid is withdrawn, filtered, well acidified with pure nitric acid, and ammonium thiocyanate added; if any signs of colouration ensue the agitation is continued until every trace of iron has disappeared. The cold solution is then filtered through a close filter-paper, and the clear bright solution is poured in a thin stream with constant stirring into an excess of a clear saturated cold solution of re-sublimed ammonium sesquicarbonate. Reversing the operation by pouring the ammonium carbonate into the lead nitrate leads to the formation of

* Further experiments are in progress with some of the least basic constituents of the yttrium group of metals.

basic lead nitrates and does not answer. The precipitated lead carbonate is allowed to subside and then washed, best by decantation with distilled water, and finally is collected on a filter of toughened paper, and further washed till about half a litre of the washings, to which a drop or two of methyl-orange solution is added, shows a decided acid reaction with two drops of normal nitric acid. It requires a considerable amount of water to remove the last traces of the ammonium carbonate, which of course is indispensable. The lead carbonate is then allowed to drain and dry in a warm place till it becomes pasty, and in this state it is removed into a wide-mouthed stoppered bottle and preserved for use. It acts much better in this moist state than when it is dried, and is more easily diffused in the solutions of the nitrates.

The following experiments selected from a great many examples are given to show the completeness of the separation effected with carbonate of lead. The purest thorium nitrate obtainable, labelled "Thorium" Nitrate Absol. Chem. Pur.," was taken. A solution of this was prepared so that 100.0 c.c. equalled 1 grm. of the crystallised nitrate.

100.0 c.c. precipitated with a slight excess of ammonia, the precipitate washed, dried, and ignited by blast-lamp, gave thoria 0.4785 grm. 100.0 c.c. of the same solution was treated with excess of the moist carbonate of lead, and frequently stirred for twelve hours; then the insoluble matter was collected on a filter, washed, and the filtrate kept. The precipitate was dissolved in the smallest possible amount of dilute nitric acid suitably diluted, and the lead removed by passing sulphuretted hydrogen. The lead sulphide being filtered off, the filtrate was boiled, evaporated somewhat, and precipitated by ammonia; the precipitate washed, dried, and ignited over the blast-lamp. The ignited precipitate weighed 0.4765 grm. The filtrate from the carbonate of lead treatment was treated with sulphuretted hydrogen in the same way; after filtering off the lead precipitate the solution was boiled to a small bulk and heated with ammonia and a little ammonium oxalate. A small precipitate was obtained which, when collected, washed, dried, and ignited, weighed 0.0015 grm.; it was of a chamois colour, and on being dissolved in hot strong sulphuric acid it gave the reactions of cerium with ammonium persulphate, and also with hydrogen peroxide in the solution rendered alkaline by ammonia. So that this trial separated at one treatment 0.15 part of ceria-yttria oxides from 47.65 parts of thoria contained in the so-called "Thorium Nitrat. Absol. Chem. Pur." This may be contrasted with the marvellously complex process of Fresenius and Hintz by which they separated ultimately 0.1357 part of ceria, neodymia, lanthana, and yttria from 46.2066 parts of thoria. Still even this mode of procedure leaves something to be desired, as the ignited thoria precipitate was not perfectly white, and it was found that this occurred because a small portion of the cerium in the thorium nitrate existed as ceric nitrate. Solutions of cerous nitrate are readily oxidised when evaporated with nitric acid. In a trial made with a solution of cerous nitrate evaporated twice to dryness on the water-bath with nitric acid of 1.520 specific gravity, nearly 50 per cent of the total amount of cerium was converted into the ceric form, and as ceric nitrate is completely precipitated by lead carbonate, the necessity of being absolutely certain that all the cerium exists in the cerous form is evident. The best method of attaining this is to heat the dilute solution with hydric sulphide, and then to boil off the excess without allowing the solution to become concentrated or highly acid.

Sulphurous acid may also be employed to reduce any ceric salt. Therefore, to separate the traces of foreign earths in commercial thorium nitrate, dissolve in water about 1 to 2 grms. per 100 c.c., pass a current of H_2S , boil off the gas completely, and keep up the amount of water

evaporated. When cold, add moist carbonate of lead, and proceed as described.

After dissolving the washed precipitate of thoria with excess of lead carbonate and separating the lead as sulphide, it is evident that it is easy to repeat the separation by adding a fresh portion of carbonate of lead. However, the amount of any foreign oxides thus separated is so minute that it is generally hardly worth the additional trouble that it entails. In these first experiments a great excess of thoria was associated with a minute amount of foreign oxides; in those to be described the amounts of ceria-yttria oxides were in some cases equal to the amount of thoria, and in some instances only traces of thoria were dealt with, mixed with a very large amount of the other earths. It was at first contemplated that the cerium-yttrium group of earths should be treated one by one to ascertain how they behave with lead carbonate when they were associated with thoria.

But it was found that this would entail a vast amount of work, and further that many of these oxides were scarcely obtainable in a state of purity, and so it was resolved to deal with them collectively, as by this means one would realise the actual conditions generally encountered in the analysis of minerals containing the rare earths. The technical working up of large quantities of monazite sands for the preparation of thoria yields as by-products, for which little use has yet been found, very considerable quantities of the salts of the cerium-yttrium group of metals, and among these a product is found in commerce under the name of "Crude Cerium Nitrate." It forms a dry nearly white granular powder with a faint rosy hue, and smelling slightly of nitric acid. A quantity of this was obtained and examined, in the first place, qualitatively. It was found to contain only faint traces of iron, calcium, or magnesium, no phosphate, chloride, or sulphate, a little free nitric acid, a small amount of thoria (0.67 per cent), about 19.4 per cent of ceric oxide, and about 19.57 of other rare earthy oxides, comprising lanthana, neo- and praseodymia, samaria, and also metals of the yttria group. It dissolved in water readily, giving a slightly opalescent solution, and when this solution was precipitated with oxalic acid it yielded oxalates of a faint rose colour, which on ignition gave oxides of a bright brown colour which amounted to 39.64 per cent on the nitrates employed. These nitrates were treated as follows:—40 grms. were dissolved in about a litre and a-half of distilled water, filtered, and the clear filtrate treated with excess of hydric sulphide. There was no sign of any heavy metals, even on standing. The sulphuretted hydrogen was then boiled off, and when cold an excess of pure moist carbonate of lead was added, and the whole kept well stirred for twenty-four hours. The precipitate was filtered off, well washed, and dissolved in the smallest possible amount of nitric acid, diluted, and the lead precipitated as sulphide; this was filtered off, washed, and the solution was concentrated to about 50.0 c.c. To this solution, when boiling, was added a hot solution of pure oxalic acid in slight excess, the whole allowed to stand twelve hours, and the oxalate washed with hot water and dried at 100° C. The oxalate was then removed from the filter-paper as far as possible into a small porcelain crucible, further dried to a constant weight at 100° C., and then weighed. 0.369 grm. of oxalate gave 0.2175 grm. of a white oxide equal to 58.94 per cent, which agrees almost exactly with the composition of thorium oxalate dried at 100° C. The oxide dissolved in sulphuric acid diluted with an equal amount of water after considerable digestion, and this solution at a suitable concentration yielded a fluid which when heated became semi-solid from the separation of the characteristic "cotton-wool sulphate," which dissolved again on cooling. When the few drops of mother-liquor which could be separated from this hot pasty mass were drained off, dissolved in water, and excess of ammonia and hydrogen peroxide added, there was a slight but distinct evidence of ceric peroxide. But when hydrogen peroxide was added to the slightly acid and rather concentrated solution, a heavy

* This sample of thorium nitrate was obtained some time ago, before the practice of adding intentionally 1 per cent of ceria was in vogue.

precipitate of thorium peroxide sulphate formed at once. So that it is clear that the great mass of the precipitate was thorium, as the composition of the oxalate shows, but that it still contained slight traces of ceric oxide, which would be entirely removed by a repetition of the treatment with carbonate of lead. However, the present object was only to obtain a solution of earth nitrates quite free from thorium. The quantity of thorium obtained from the nitrates in this manner amounted to 0.602 per cent on the original nitrates, showing that the commercial extraction of the thorium had failed to remove this amount.

(To be continued).

ON TERBIUM AND SOME OF ITS COMPOUNDS.

By EMMA A. POTRATZ.

THE metal which is the subject of this paper was discovered and described in 1843, under the name of erbium, by Mosander, confirmed by Berzelius, Scherer, and others. Later on Bunsen and several other chemists denied the discovery of Mosander and applied the name *erbium* to another metal also discovered by him. Delafontaine and Marignac demonstrated simultaneously the individuality of the Swedish chemist's erbium; but in order to avoid confusion, they proposed that the name *terbium* be transferred to the erbium of Mosander, which was accepted. Since 1880 terbium has not been the object of extended researches, not to my knowledge at least. As will be seen, the results here described confirm and extend those of the two chemists of Geneva and Chicago.

Terbium belongs to that large family known as the rare metals, rare earths, cerite and gadolinite metals, &c., having three characteristics in common:—that their oxides, powerful, salifiable bases, cannot be reduced by ordinary means, and form salts possessing a more or less sugary and astringent taste. It acts like the rare earths with oxalic acid, the alkaline oxalates, potash, potassium sulphate, in addition to which it has characteristics of its own, which leave no doubt about its individuality as an element, such as the lack of colour of its solutions, its specific gravity, molecular weight, spectrum, &c.

The salts of the members of the didymium and erbium groups are coloured and show characteristic absorption spectra, which is not true of the *terbia* compounds.

Lanthanum and yttrium differ by their beautiful spectrum of brilliant lines, their atomic weight, the whiteness of their oxides, &c.

The solutions and solid salts of samarium are yellow and give a specific absorption spectrum.

Terbium and decipium (the so-called gadolinium of some chemists) have different atomic weights and spectra.

Terbium oxide, Tb_2O_3 , is a brownish-orange powder like some varieties of ochre. Its specific gravity is 6.27. The shade of the colour varies from a lighter to a darker tint according to whether the oxide was prepared from the formate, the acetate, or the carbonate, &c. It is a very powerful base, equal in that respect to didymium oxide. It really combines with moderately dilute acids, with a very slight evolution of gas, even after it has been recently and strongly ignited. That is due to a very incomplete sur-oxidation. A very small quantity of water is formed when *terbia* is heated in a current of H. After that treatment terbium oxide is white and opaque. The oxide, after that calcination, dissolves readily in acids. A moderate calcination in an open dish restores the original colour of the reduced *terbia*, unless it has been ignited at a very high temperature. An unsuccessful attempt was made to prepare a higher degree of oxidation of terbium.

A very cold solution of terbium sulphate was mixed with hydrogen peroxide and precipitated by pure ammonia. The precipitation was attended by a slight evolution of O. The gelatinous hydrate assumed a very pale greenish colour by drying at the ordinary temperature. The

analysis of that product showed it to be a mixture of terbium hydrate and a very small proportion of a higher oxide not in definite proportions. Moreover, in spite of a careful washing it retained some basic sulphate, for when dissolved in dilute HCl, after reduction in H, it emitted a gas with a strong odour of H_2S . Terbium hydrate, $Tb_2O_3 \cdot 3H_2O$, is like cerous hydrate in the air. It obstinately retains a small quantity of acid, even when the precipitation has taken place in the presence of a strong excess of ammonia. It draws the carbonic acid of the air; combines easily with the acids. It contracts very much by drying and becomes quite opaque. It contains 13.23 per cent of H_2O , which is expelled by a strong heat and leaves Tb_2O_3 in dark brownish-orange lumps.

Terbium has such a tendency to make basic salts that it is not advisable to try and make its hydrate by throwing it down by ammonia. A better way is to pour the terbium solution into an excess of caustic potassa, &c.

Colloidal Compounds.

Like yttrium acetate, the corresponding terbium salt is capable of producing a colloidal compound which is evidently a soluble hydrate, although it always retains a very small proportion of acetic acid, as Delafontaine has shown to be also the case with colloidal yttrium hydrate. Ultimately the solution of the colloidal terbium hydrate coagulates and settles at the bottom of the bottle. After a strong calcination it leaves Tb_2O_3 with its natural intense colour.

Terbium Chloride.

This compound is easily obtained by dissolving *terbia* in moderately dilute HCl and evaporating the clear colourless solution. Owing to its very great solubility it crystallises with difficulty. The tabular crystals are deeply truncated, rectangular octahedra.

By the application of heat it loses its water and melts into a pasty mass, which seldom re-dissolves completely in water owing to the formation of a more or less copious residue of oxychloride. That is why no attempt has been made to obtain free Tb by decomposition with K or Na. The electric furnace which has given such remarkable results in the hands of Moissan, would probably give a purer product.

Terbium Bromate, $Tb_2O_3 \cdot 3Br_2O_5 \cdot 18H_2O$.

This was obtained by neutralising bromic acid with *terbia*. It crystallises spontaneously and forms colourless, transparent glistening crystals, not deliquescent, containing 18 molecules of water. They are hexagonal, deeply truncated pyramids, probably isomorphous with didymium bromate.

Analysis.

	Found.
Tb_2O_3 25.33	25.60
18 aq. 23.17	23.00
$3Br_2O_5$ 51.50	

Terbium Perchlorate.

Perchloric acid neutralised by *terbia* gives a clear colourless solution. After evaporation, the perchlorate is left in very small crystals which soon re-dissolve in the mother-liquor. This solubility is so great that no attempt was made to analyse that salt. The perchlorate is also very soluble in alcohol.

Terbium Carbonate.

A solution of pure crystallised ammonium carbonate was used to precipitate a solution of terbium perchlorate. The precipitate was somewhat gelatinous, white, and settled readily. An excess ammonium carbonate did not re-dissolve it. Upon standing in water it did not assume a crystalline appearance, and did not change colour on exposure to air. It dried exceedingly slowly in the air. The analysis gave—

CO_2 22.52
Tb_2O_3 61.76
Aq. (by diff.) 15.72

which corresponds to the formula of a normal carbonate with six molecules of water. By desiccation at 100° C. that salt loses also some CO₂. The calculated amount of terbia is nearly 59.6 per cent. I have found 61.75, and 63.21 per cent from samples kept in open air from one to three weeks.

Terbium Acetate, Tb₂O₁₂H₁₈O₁₂+8aq.

Terbia readily dissolves in warm moderately dilute acetic acid. The colourless solution yields fine transparent colourless crystals. These crystals are four-sided plates with bevelled edges and sometimes with truncated corners, isomorphous with yttrium and didymium acetate. They contain 8 molecules of water, which they lose at a few degrees above 100° C. 100 parts water dissolve 9 parts of crystals at 60° C.

Analysis.—100 parts of crystals, crushed and pressed in filter-paper, gave 18.17 of water and 43.96 of Tb₂O₃. The theory requires 17.18 of water and 44.03 of base.

Terbium Formate.

As this salt plays a very important part in the separation of terbium, especial care was taken to obtain it as free as possible from the formates of yttrium, didymium, &c. Its solubility is 1.8 in 100 parts of water, or approximately 54 parts water dissolves 1 of formate, which is the average of two closely agreeing determinations. Delafontaine had found that solubility to be about 1 in 35 parts of water, but later on the spectroscope showed that his product still retained some yttrium formate. It is an amorphous, white salt deposited in compact crusts on the sides of the evaporating dish or a white powder. By ignition, it retains its form without swelling up as yttrium formate does. It is anhydrous.

Terbium Meconate.

This salt, which was obtained by neutralising a warm but not-boiling solution of meconic acid with terbium carbonate, is an insoluble whitish compound which contains 83.80 per cent of base. The formula for an anhydrous tri-basic meconate requires 84.15 per cent. terbia. The meconate when strongly heated, softens, swells up, and turns black. Finally, in the presence of air, all the carbon is burned, leaving nearly 84 per cent terbia.

Terbium Citrate.

Terbia citrate was obtained by neutralising a concentrated cold solution of citric acid by terbium carbonate. The clear colourless solution of that salt leaves by spontaneous evaporation a varnish-like transparent residue without any appearance of crystallisation. The solubility of the citrate decreases with the temperature. At about 45° the solution becomes cloudy, the cloudiness increases as the thermometer runs higher until 85° or so, where the curdy precipitate becomes pulverulent and the thermometer remains stationary for several minutes. When the liquid is cold again, the citrate re-dissolves without leaving any residue. While drying, the separated citrate forms a transparent coating on the sides of the filter, and the filtrate still retains much dissolved citrate, which is thrown down by means of strong alcohol.

Terbium Carbide.

Calcined in a closed crucible, the organic salts of terbium, especially the formate and the acetate, leave a black, charcoal-like residue which consists of terbium carbide with a small proportion of oxide and free carbon. The product is purer if the decomposition is carried on in a tube through which passes a stream of pure dry H₂. The residue catches fire and burns like tinder when it is thrown on a table. That product is stable in the air, if it is allowed to cool in an atmosphere of H₂. Very dilute acids dissolve very little of terbium oxide and leave the carbide TbC₃ between 98 and 95 per cent pure. The carbide thus obtained does not acquire the metallic lustre by rubbing it in an agate mortar. A better way to obtain that and the

similar compounds of the other metals would be by using the electric furnace as M. Moissan does.

Extraction.

The terbia used in my experiments was extracted chiefly from samarskite, in the shape of mixed earthy fluorides decomposed by sulphuric acid, and transformed into oxalates and lastly into nitrates as usual. After the separation of thoria and uranic oxide, the solution of the mixed earths was separated into compounds of the cerium and the yttrium groups. The latter treated thrice with sodium sulphate afforded a further separation into insoluble sodium double sulphates and soluble ones. Terbia was thus concentrated into the former, extracted, re-dissolved in nitric acid, and thrown down in fractions by oxalic acid, as usual. The latter treatment repeated several times gave a strongly coloured base after ignition of the oxalate. That base was then subjected to a number of treatments by formic acid until no yttria was left, as shown by the spectroscope; a small quantity of didymium concentrated in the final product was removed by a last treatment with potassic sulphate, which reduced it to less than one part in 10,000.

Atomic Weight of Terbium.

Apparently the best method for the determination of the atomic weight of the rare earths is by the synthesis of the sulphate. Wyruboff was the first, I believe, to show the practical difficulties attending the application of that method to some of the earths; I met the same in the case of terbium.

The complete expulsion of the excess of sulphuric acid takes place at a temperature so near that at which the normal sulphate commences to decompose, that the exact moment at which to stop the heating of the salt is hard to ascertain. Therefore I have confined myself to the analysis of the dehydrated sulphate by precipitation with ammonium oxalate. One sample made from an earth spectroscopically free from Y, Dp, Yb, and Sm gave Tb₂O₃ = 355.8; Tb = 153.9.

Water	19.20
Tb ₂ O ₃	48.24
SO ₃ (diff.)	32.56

100.00

Another sample gave Tb = 154.2. A sample of well purified formate gave 61.60 per cent of base (Tb = 154).

Carefully dehydrated crystals of acetate left 53.65 per cent of base (Tb = 153.1).

No serious error will be made by adopting 154.

The description of the sulphates, double sulphates, and nitrates will be given in another paper with a more extended report on the atomic weight of terbium.

Chicago (U.S.A.), June 3, 1905.

NOTE ON THE ESTIMATION OF FAT IN MILK BY THE LEFFMANN-BEAM PROCESS.

By L. DE KONINGH.

In using this method it is sometimes impossible to get an accurate reading, owing to the formation of a fluffy substance between the fatty and acid layers. This fluffy matter may, however, be readily removed and broken up by means of a very thin metallic wire.

"Glucinum" v. "Beryllium."—M. Delafontaine draws our attention to the fact that Fourcroy settled this controversy in favour of "glucinum" when he said, in the second volume of his "Système des Connaissances Chimique," that it was crystallography which prompted Haüy to request Vauquelin to re-analyse emerald and beryl, resulting in the discovery of a new earth for which Vauquelin, Guyton, Chaptal, and Fourcroy adopted the name Glucine. Previous to Vauquelin's work, Bindheim and Klapproth had mistaken glucina for alumina.

ON THE SPECTRA OF TERBIUM AND OTHER METALS OF THE RARE EARTHS.

By M. DELAFONTAINE.

IN spite of the efforts of many chemists, our knowledge of the rare metals is still in a state of great confusion. The spectroscope, so useful in other lines, has led to widely different conclusions; not that the instrument itself is unreliable, but because it was applied to the study of evidently impure materials, and not always used under the proper conditions.

If there is one element whose identity is well established in the minds of many, that is yttrium. As long ago as 1878, however, I pointed out various facts showing the existence of at least another metal in it. But because the spectroscope seemed to go against my conclusions they were not accepted. That was natural enough: M. Thalén's famous work was supposed to have been done with material of the greatest purity; Bunsen's work was done with an instrument of low dispersive power (it did not separate the sodium lines) and his yttria was manifestly impure, as was proved later.

Thalén first mapped out 86 yttrium lines, but reduced them later to 43. (He has also reduced the number of his lines above 600 units from 19 to 11). Then came Rowland's splendid revisions, in which he gives 42 wave-lengths in the region covered by Thalén (from 4084 to 643'52). But there are in the Upsala physicist's table 23 lines not in Rowland's, and 18 in Rowland's not in Thalén's. In that comparison I call identical those lines not more than 1·0 unit apart (such as 4422'00 and 4422'8, or 4374'0 and 4375'1).

The causes of error are such that an absolute agreement is not to be expected in every case. However, the skill of each of them justifies the smallness of the differences adopted by me. Thus, spectroscopically, there is an *old* and a *new* yttrium.

My own investigations were carried on during the last eight or nine years with a one-prism spectroscope of a comparatively low dispersive power, but mostly with a spectrometer with a Rowland's opaque flat grating of 14,438 lines to the inch (about 26,000 lines altogether).

The graduated circle allows readings up to 10'', D₁ and D₂ are shown about 2' apart to the 2nd order spectrum. The observed spectra were from different chlorides extracted from gadolinite, samarskite, and fergusonite, freed as much as possible from terbia and the earths of the cerium group. My own readings were all verified by Miss Potratz. To obtain good results, the condensed spark must be as strong as possible and the chloride solution near the point of saturation. But, nevertheless, some regions present a great variability under conditions apparently identical.

A number of times have I obtained spectra almost identical with Thalén's, and when I compare my results with those of Rowland's I am forced to the conclusion that Thalén's last yttrium was a mixture of at least two metals. I separated long ago a metal which I called Philippium, the not completely pure chloride of which gives about 50 lines not in Rowland's yttrium spectrum; the majority of them are seen in the old Thalén's yttrium. Of the lines of my philippium five belong perhaps to terbium, three to yttrium, and three doubtfully to scandium.

Under the best conditions the spark spectrum of terbium appears as a narrow continuous spectrum, faint at the red end but growing more intense towards the violet. That luminous coloured band is crossed by a great many bright lines; two, quite fugacious, are in the yellowish end of the orange, very few in the yellow and yellowish green; they increase in numbers and brilliancy from the green to the violet, where they are so close together and variable in intensity that it is possible to measure only the most conspicuous ones (in the green and blue).

The following is a list of some of the appropriate wave-lengths observed in the region between 600 and 430:—

597'957		506'236
582'604		505'594
566'2		505'4
550'623		502'93
539'177		498'87
529'470		488'05
525'038		481'5
524'5		466'42
520'066	Double	464'2
518'928	Faint	464
518'00		460'118
514'820	Strong	450'56
512'10		434'32
510'48		431'63
516'16		438'28
507'0		432'5

None of the above lines occurs in the yttrium (Rowland's), samarium, decipium (gadolinium) spectra.

The reversal of spectral lines has been observed in numerous instances. Generally the reversed lines are the brightest of the spectrum. Barium, bismuth, cadmium, copper, iron, &c., afford good illustrations of that phenomenon.

I have once observed the reversal of the Di and Sm spectra under conditions different from those described by Bunsen. A solution of terbium chloride containing a very small proportion of Di and Sm (less than 1 per cent) was being sparked in front of a one-prism spectroscope. The spectrum appeared as a narrow band of light, almost continuous but faint, crossed by numerous lines of variable intensity. When the current lost some of its strength so did the bright lines, but there appeared also about thirteen narrow sharply limited black lines, which occupied the position of so many coloured lines of Di, Tb₃, and Sm₃. Another interesting feature: the liquid below the spark assumed a yellow colour and showed—above the luminous band—the absorption lines of the two metals, but broader, with their usual haziness at the edges. The space above the solution exhibited a fine lavender coloured bloom.

Chicago (U.S.A.), June 3, 1905.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 14th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MR. G. W. T. Horrod was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Harry Dunlop, Cragdarroch Cove, Dumbartonshire; Eric Haydn-Morris, care of Messrs. G. Mowling and Son, Footscray, Melbourne, Victoria.

The PRESIDENT announced that it had been decided by the Council that the ordinary meetings of the Society shall be held during the ensuing Session on the first and third Thursdays at 8.30 p.m.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Edward Williams Bealey, B.A.; William J. Bees, B.Sc.; Joseph Bennett; William Robert Bousfield, M.A., K.C., M.P.; Eric William Campbell; William Beaverly Cowie; William Walpole Day, B.Sc.; Ralph Emerson De Lury, M.A.; Robert Donald, M.A., B.Sc., M.R.C.S., L.R.C.P.; Ernest Lyle Carman Forster, M.A.; Herbert Henstock, B.Sc.; William John Jarrard, B.Sc.; Arthur Walter Mason, B.Sc.; Frederick Wilson Montrose Ross; James Steger, B.Sc.; William Bradshaw Tuck; John William White; William James Wren.

Of the following papers, those marked * were read :—

*121. "Influence of Various Sodium Salts on the Solubility of Sparingly Soluble Acids." By JAMES CHARLES PHILIP.

That magnesium hydroxide is more soluble in ammonium chloride solutions than in pure water is due, according to one current explanation, to the formation of undissociated ammonium hydroxide, and the consequent removal of hydroxyl ions, this leading to the solution of more hydroxide. If this is so, then conversely the solubility of sparingly soluble acids should be increased in the presence of sodium salts of weak acids. This is found to be actually the case, and the influence of sodium formate, acetate, and butyrate, on the solubility of cinnamic, benzoic, salicylic, and *o*-nitrobenzoic acids has been determined at 26.4°. It is to be expected on theoretical grounds, and the expectation is confirmed by the experimental results, that the extent to which the solubility of a given sparingly soluble acid is increased by the presence of the sodium salt NaA will depend on the strength of the acid HA. If the concentration of the sparingly soluble acid in the saturated solution is plotted against the concentration of the added salt (NaA, NaA', NaA'', &c.), it is found that the order of the curves so obtained is the order of strength of the acids HA, HA', HA'', &c. Further, the increase of solubility of cinnamic acid, for example, in solution of NaA of known concentration, as compared with its solubility in pure water, can be calculated in good agreement with experiment when the solubility product for cinnamic acid and the dissociation constant of the acid HA are known.

*122. "The Dielectric Constants of Phenols and their Ethers Dissolved in Benzene and *m*-Xylene." By JAMES CHARLES PHILIP and DOROTHY HAYNES.

Evidence was brought forward some time ago by one of the authors (Philip, *Zeit. Physik. Chem.*, 1897, xxiv., 18) showing that the dielectric constant of an alcohol calculated from the dielectric constant of its benzene solution decreases as the concentration of the alcohol decreases, and is in all cases less than the directly determined dielectric constant of the pure alcohol. This behaviour, connected probably with the associative tendency of the alcohol molecules, has now been observed also in the case of phenols. The phenomenon is well marked in the case of phenol itself, but less distinct in the case of the cresols; indeed, the dielectric power of *o*-cresol in benzene solution seems to be nearly independent of the concentration. The phenol ethers, in which the associative tendency has been got rid of by obliterating the hydroxy-group, exhibit an almost dielectric behaviour in benzene solution. It is noteworthy that the introduction of a methyl group at any point in the ring lowers the dielectric constant of anisole, the lowering effect, however, of the methyl group being much greater in the ortho-position than in either the meta- or para-position.

DISCUSSION.

Sir WILLIAM RAMSAY inquired whether Dr. Philip's measurements threw any light on the fact that the molecular weight of alcohol in benzene solutions may rise as high as 230. Was this due to polymerisation of the alcohol or to a compound of alcohol with benzene?

Dr. PHILIP said that although the dielectric property of alcohol in benzene had been found to diminish with dilution in an analogous manner to the molecular weight, no evidence had been obtained bearing on the point referred to by Sir William Ramsay.

*123. "Synthesis by Means of the Silent Electric Discharge." By JOHN NORMAN COLLIE.

When pure ethylene was submitted to the action of the silent electric discharge in a vessel cooled to -20°, polymerisation occurred, and a liquid was produced together with some hydrogen gas. In one experiment, 210 c.c. of ethylene gave about 40 c.c. of hydrogen.

Ten grms. of the liquid produced by the polymerisation of ethylene were fractionated. The fractions collected, and their analyses were as follows:—

	100°.	100—150°.	150—200°.	200—250°	Residue.	Distilled residue.
C ..	83.4	85.3	85.8	86.0	87.7	87.7
H ..	16.0	15.3	14.3	14.0	12.4	12.3

The first fraction was very small; most of the distillate collected in the two fractions 100—150° and 150—200°, the chief part boiling between 130° and 170°. The residue left in the flask was a dark resinous substance, which, on heating, smelt of burnt indiarubber; this product weighed 4 grms., or two-fifths of the whole.

The decrease in hydrogen and increase in carbon in the above analyses is interesting; olefinic hydrocarbons, C₄H₂₄, require C=85.7, H=14.3; C₂₀H₃₄ requires C=87.7, H=12.3 per cent.

These various fractions were oxidised by means of potassium permanganate solution in the cold. After filtering off the precipitated manganese oxide, the solution of potassium salts was acidified; a strong odour of either valeric or caproic aldehyde was at once produced in the case of the two fractions (100—150° and 150—200°). These aldehydes were distilled in steam, and oxidised with silver oxide. The silver salt gave, on analysis, Ag=48 per cent, which is equivalent to an acid of molecular weight 118, that of caproic acid being 116.

Ethylene was also mixed with carbon monoxide, and submitted to the silent electric discharge, when aldehydes were formed in small quantity. Formaldehyde and acrolein were both probably present, but the chief condensation that occurred was that of the ethylene itself to form hydrocarbons having high boiling-points.

The facts that are of especial interest are that ethylene under the influence of the silent electric discharge at the ordinary temperature will not only unite with carbon monoxide, but will also polymerise, yielding a series of complicated hydrocarbons; the chief substances formed boil at about 150—160°, and apparently approximate in composition to C₁₀H₂₀; moreover, further condensation means loss of hydrogen and the formation of compounds approximating both in properties and composition to the terpene derivatives. On oxidation, the olefinic hydrocarbons break down, yielding compounds containing about six carbon atoms in the molecule.

DISCUSSION.

Mr. HARCOURT referred to experiments on ozone by Sir B. Brodie, in which the oxygen exposed in a Siemens tube to the silent discharge was mixed with a large proportion of carbon dioxide, the idea being that ozone might be protected during its formation by dilution with carbon dioxide, and obtained afterwards in a concentrated form by absorption of the diluent. The results, however, showed that carbon dioxide was decomposed and ozone formed from it; moreover, a brown coating was deposited on the glass, this product being readily soluble in water. This experiment seemed to be an illustration of Dr. Collie's view that the syntheses which plants effect under the influence of sunlight, forming complex products out of carbon dioxide and water, may be to some extent paralleled by the action of the silent discharge.

Prof. TILDEN reminded the author that experiments of the same character and having similar results had already been carried out by Berthelot (*Journ. Chem. Soc.*, 1876, ii., 596).

The PRESIDENT considered that not the least interesting part of Prof. Collie's paper was the fact that he had succeeded in obtaining a sufficient quantity of the synthesised products to enable him to give definite and quantitative information as to their nature. Most of the workers who had studied the synthetical action of the silent electric discharge had hitherto only given qualitative results. With reference to the polymerising action of this discharge, he (the President) mentioned that some years ago, in conjunction with Mr. R. J. Strutt, he had made some experiments having for their object the possible combination of argon with acetylene. No combination was observed, but the polymerising action of the discharge on

the acetylene was very obvious, an accumulation of tarry and resinous products being obtained, but these were not further examined, as practically the whole of the argon originally mixed with the acetylene was recovered at the end of the experiments. With respect to photosynthetic processes, he thought it might be of interest, in view of the modern developments of radio-activity, to call attention once again to the older work of Fay, and of Seekamp, who states that photochemical decompositions are in many cases promoted by the addition of uranium salts to the solutions. This raises the question whether the energy, which must be supposed to be liberated on the "disintegration" hypothesis of the uranium atom, may not play a part in such photochemical processes.

*124. "The Ultra-violet Absorption Spectra of Aromatic Compounds. Part I. Benzene and certain Mono-substituted Derivatives." By EDWARD CHARLES CYRIL BALY and JOHN NORMAN COLLIE.

The ultra-violet absorption spectra of benzene and of some of its mono-substituted derivatives were described. It has been found that benzene presents seven separate absorption bands, and it was shown how the formation of these may be accounted for by attributing each one to a separate and distinct process of dynamic isomerism connected with the linking changes within the benzene molecule. In the case of the mono-substituted derivatives of benzene, it is shown how their absorption spectra may be arranged in types, and it appears that each type corresponds either to complete saturation or to the nature and position of unsaturated atoms in the substituent group. The presence of an unsaturated atom in the α , β - or γ -position in the side-chain thus produces a particular type of absorption. When the unsaturated atom is present in the δ -position, it is apparently removed too far from the nucleus to exercise any effect, with the result that the same absorption spectrum is obtained as if the side-chain were completely saturated.

*125. "The Ultra-violet Absorption Spectra of Aromatic Compounds. Part II. The Phenols." By EDWARD CHARLES CYRIL BALY and ELINOR KATHARINE EWANK.

The ultra-violet absorption spectra of anisole and phenetole are found to differ from that of phenol; in the former cases, the single absorption band given by phenol is sub-divided near its head into two bands. The absorption band produced by the dynamic isomerism existing in solutions of acetylacetone and similar tautomeric substances of the aliphatic series occupies very nearly the same position as the band given by phenol. The existence of a similar type of dynamic isomerism in the case of phenol would therefore explain the difference between the spectra of phenol and its ethers. The presence of this kind of tautomerism, that is, a labile hydrogen atom, in phenol is proved by the influence of acid and alkali on the spectrum of this substance. Just as in the case of certain aliphatic tautomeric compounds, the position of the absorption band is shifted towards the red on the addition of sodium hydroxide, whilst the addition of acid tends to restrain the dynamic isomerism. The results obtained with the three dihydroxybenzenes, the three cresols, and *p*-aminophenol support the view that similar tautomerism exists in these substances.

*126. "Association in Mixed Solvents." By GEORGE BARGER.

The association which many hydroxylated substances exhibit in some solvents (benzene, chloroform) does not occur in others (alcohol, acetic acid), probably because the latter form loose molecular compounds with the solute according to the law of mass action (Abegg, *Zeit. Anorg. Chem.*, 1904, xxxix., 330). In dilute solutions, the concentration of the solvent is large compared with that of the solute, and if the solvent is dissociative its influence predominates. The present investigation deals with cases in which the concentration of the dissociative solvent was reduced by mixing it with an associative one.

The dissolved substances were acids, alcohols, phenols,

and oximes. Dilute solutions of these were made in mixtures of toluene, benzene, chloroform, or carbon tetrachloride with one of the following dissociative solvents:—Pyridine, acetic acid, ethyl acetate, methyl acetate, ethyl formate, ethyl alcohol, methyl alcohol, and acetone. The molecular weight of the solute was determined by the author's microscopic method (*Trans.*, 1904, lxxvi., 286), this process being particularly suited for work with mixtures.

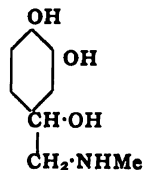
The results are in general agreement with what might be expected from mass action according to the above theory. The molecular weight is normal in nearly all the mixtures, and association only persists when the percentage of the dissociative solvent is very small.

The esters are the least powerful of the dissociative solvents examined, which is in accordance with their behaviour in other respects. For instance, as the result of a study of the boiling-points of homologous series, Young places the esters between associated and non-associated liquids (*Phil. Mag.*, 1905, [6], ix., 1).

According to Lachman (*Journ. Am. Chem. Soc.*, 1903, xxv., 50), brown solutions of iodine owe their colour to the formation of loose molecular compounds between solute and solvent. If equal volumes of an alcoholic and a chloroform solution containing equal quantities of iodine are mixed, the colour of the mixture is not intermediate between that of the component solutions, but is more like that of the alcoholic solution. This experiment serves to illustrate the mass action effect of the solvent.

*127. "Synthesis of Substances Allied to Epinephrine." By GEORGE BARGER and HOOPER ALBERT DICKINSON JOWETT.

The authors have attempted to synthesise a compound having the formula—

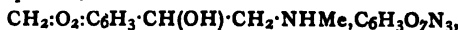


which was proposed by one of them (*Trans.*, 1904, lxxv., 192) for epinephrine (adrenaline), the active principle of the suprarenal gland.

Although the methylene and dimethyl ethers were prepared, the dihydroxy-base could not be isolated.

The constitution of the ether bases was proved by their oxidation to piperonylic or veratric acid respectively. The dihydroxy-base could not be obtained from the ethers, although indications of the formation of a substance having the chemical and physiological properties of epinephrine were obtained by the action of dilute hydrochloric acid at 150° on the methylene ether.

The following compounds were prepared and described:— α -3 : 4-methylenedioxyphenyl- α -*β*-dibromoethane, $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CHBrCH}_2\text{Br}$, needles, m. p. 82–83°; α -3 : 4-methylenedioxyphenyl- β -bromo- α -hydroxyethane, $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH(OH)CH}_2\text{Br}$, long needles, m. p. 107–108°; β -3 : 4-methylenedioxyphenyl- β -hydroxyethylmethylamine picrate,—



yellow needles, m. p. 178°; the corresponding base and platinichloride are amorphous; 3 : 4-dimethoxystyrene, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH:CH}_2$, colourless liquid boiling at 120–125°/10 m.m.; α -3 : 4-dimethoxyphenyl- α -*β*-dibromoethane, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CHBrCH}_2\text{Br}$, needles, m. p. 102°; α -3 : 4-dimethoxyphenyl- β -bromo- α -hydroxyethane, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH(OH)CH}_2\text{Br}$, long needles, m. p. 68°.

The corresponding methylamine base could not be crystallised, nor could any crystalline salt be obtained.

The piperonyldibromide (m. p. 160°) described by Mameli (*Gazzetta*, 1904, [1], xxxiv., 358) is really the *dibromohydrin*, $\text{CH}_2\text{O}_2\text{C}_6\text{H}_2\text{BrCH(OH)CH}_2\text{Br}$, and has been obtained by the action of bromine water on the bromo-

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The electrolytic conditions employed were such as are generally used for preparing persulphuric acid, namely, moderately concentrated sulphuric acid and a high anode current density. By the electrolytic method, the catellagic acid obtained is purer than when potassium persulphate and sulphuric acid are employed. The reaction is being further studied, and will be extended to other hydroxybenzoic acids.

CORRESPONDENCE.

RADIUM.

To the Editor of the Chemical News.

SIR,—Some years ago Professor Japp, in an Address to the Chemical Section of the British Association, pointed out that whilst in many cases it had been found possible to synthesise inactive separable mixtures of dextro- and lævo-isomers, as well as the inactive inseparable meso-forms, yet in every case where a separation into the active components had been effected, or when either the dextro- or lævo-compound had been separately obtained, such had been brought about by the direct or indirect action of life. The recent experiments with radium, in relation to spontaneous generation, suggest that it might be worth while to institute experiments with the object of ascertaining whether a racemoid mixture of isomers can be separated into the dextro- and lævo-components with the help of radium.—I am, &c.,

L. PARRY.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 23, June 5, 1905.

Preparation and Properties of Thorium Chloride and Bromide.—H. Moissan and M. Martinsen.—Thorium chloride (ThCl_4) and thorium bromide (ThBr_4) can be easily prepared by the action of chlorine or bromine on thorium metal. These compounds, however, in an anhydrous state, whether as liquid or vapour, rapidly attack glass and porcelain, and this property renders their preparation in a perfectly pure state very difficult. It also causes a determination of their vapour density to be not altogether accurate. On the whole these two compounds possess general properties very similar to other compounds belonging to this group.

Property of Tin-aluminium, Bismuth-aluminium, and Magnesium-aluminium Alloys.—H. Pécheux.—The author investigates the conditions under which tin-aluminium, bismuth-aluminium, and magnesium-aluminium alloys decompose water.

Action of Oxygen on Cæsium-ammonium.—E. Rengade.—The rapid oxidation of cæsium-ammonium when dissolved in an excess of ammonia gives the whitish rose-coloured oxide Cs_2O_2 , the yellow oxide Cs_2O_4 , and an intermediate dark brown oxide, Cs_2O_3 . All these are crystallised in microscopic crystals. If the oxygen is allowed to act a little at a time in such a manner as to retard the decoloration of the ammonium metal, the latter reacts on the binoxide formed, giving the amide and a hydrate of the protoxide.

Pyranic Phenols.—R. Fosse and A. Robyn.—Dinaphthopyryl bromide and dinaphthopyranol can react several times on a single molecule of polyphenol. The authors obtain a dipyril-diphenol with resorcin and a tripyryl-triphenol with pyrogallol. In these phenols one atom of pyranic oxygen corresponds to each hydroxyl, and they are insoluble in aqueous alkalis and soluble in alcoholic alkalis.

New Reagent for the Detection of Aconitine.—E. P. Alvarez.—Already inserted.

Dilatation and Density of some Gases at High Temperatures. Application of this to the Determination of their Molecular Weight.—Adrien Jaquero and F. Louis Perrot.—The authors find the coefficient of expansion between 0° and 1067° of nitrogen, air, oxygen, carbonic oxide, and carbonic acid gas. By applying these numbers they then calculate the density of the gases at 1067° and their molecular weight with regard to oxygen to be—O = 32, N = 28.0155, CO = 28.009, CO_2 = 43.992.

Osmotic Pressure of Colloidal Solutions.—J. Duclaux.—With certain modifications, the author finds that all the laws relating to ordinary solutions apply equally well to colloidal solutions. From a purely qualitative point of view, the existence of an osmotic pressure tending to produce an expansion of the system explains the indefinite stability of such solutions. On the other hand, it is certain that the semi-permeable membranes formed of colloids, particularly the cellular membranes of living organisms, have not the inertia with regard to osmotic changes which is generally attributed to them.

Bulletin de la Société Chimique de Paris,
Series 3, vol. xxxiii., No. 1.

Research on the Decomposition of the Alkaline-earthly Carbonates by the Alkaline Chlorides in the presence of Water.—H. Cantoni and G. Goguelia.—Already noticed.

Solubility of some Metallic and Earthy Succinates in Water.—H. Cantoni and D. Diotalevi.—A long paper, containing many tables and diagrammatic curves, not suitable for abstraction.

Stimulative and Paralyzing Influences of certain Bodies in the Production of Rust.—L. Lindet.—Already noticed.

The Alcoyl-allyl Ketones.—E. E. Blaise.—Already noticed.

Migration of the Ethylenic Bond of the Alcoyl-allyl Ketones.—E. E. Blaise.—Already noticed.

Oxidation of Acetol.—André Kling.—Already noticed.

Constitution of Cyanide of Allyl.—R. Lespieau.—When we leave bromide of allyl, cyanide of potassium, and water in contact for a month at the ordinary temperature, we obtain a nitrile, viz., cyanide of allyl, $\text{C}_4\text{H}_5\text{N}$, to which it seems natural to attribute the formula $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CN}$. Still, at the present time most text-books of chemistry give cyanide of allyl as $\text{CH}_3-\text{CH}=\text{CH}-\text{CN}$, a formula first proposed by Kekulé. The author thinks that, in this paper, he has shown that it is necessary to return to the first formula.

The Hydrosulphites of the Aromatic Bases.—A. L. Lumière and A. Seyewetz.—The possibility of obtaining pure hydrosulphite of soda has enabled the authors to prepare various compounds with certain aromatic bases, which appear to be hydrosulphites of these bases. The compounds described were prepared particularly with regard to their properties as photographic developers. The preparations were—(1) Hydrosulphite of diamidophenol; (2) hydrosulphite of diamidoresorcin; and (3) hydro-

sulphite of triamidophenol. Hydrosulphite of paraphenylenediamine and of the aromatic monamines were also prepared. On the other hand, the simple and substituted monamine phenols, such as paramidophenol, did not give similar compounds.

The Nitrophenylcyanamides.—P. Pierron.—The nitrophenylcyanamides are obtained easily by the action of bromide of cyanogen on the corresponding nitranilines when operating in warm hydro-alcoholic solution. The method of procedure varies slightly from one nitraniline to another, according to the more or less great resistance of the base to the cyanised reagent, and according to the sensitiveness of the cyanamide obtained to the action of the hydrobromic acid given off. The bodies obtained have the same general characteristics as the aromatic cyanamides already described by Hoffmann, Voltmer, and others: fairly marked acid properties, easy transformation into monosubstituted ureas under the influence of acids, the existence of a benzoylised derivative, a tendency to polymerisation manifested by the solidification of these cyanamides after they have been kept melted for some time, with the formation of very difficultly fusible bodies.

Synthesis of Alcohols in the Cyclohexane Series.—Paul Sabatier and Alph. Mailhe.—Already noticed.

Correction on the Subject of Azodiphenylmethane.—P. Freundler.—The author finds, in a continuation of his research on the purification of benzene-o-azo-benzyl alcohol by distillation, that the product which he looked upon as azodiphenylmethane was in reality a molecular combination of azobenzene and phenylindazol.

Research on the Action exercised by different Physical and Chemical Agents on the Gluten of Wheat Flour. Estimation of this Element.—E. Fleurent.—As a result of a long research, the author concludes that chemical analysis has shown that gluten is a definite element of wheat flour, and that its mechanical extraction can be performed integrally and without loss. Distilled water and chloride and sulphate of calcium cause a loss in the estimation of gluten; prolonged washing also causes a loss of weight, and this loss is such as to bring the composition to 25 of glutenine and 75 of gliadine.

Estimation of Phosphoric Acid in Alimentary Substances.—E. Fleurent.—Inserted in full.

Constitution of Ricinine.—L. Maquenne and L. Philippe.—Already noticed.

Coloured Reaction of Cotton-seed Oil.—G. Halphen.—Inserted in full.

NOTES AND QUERIES.

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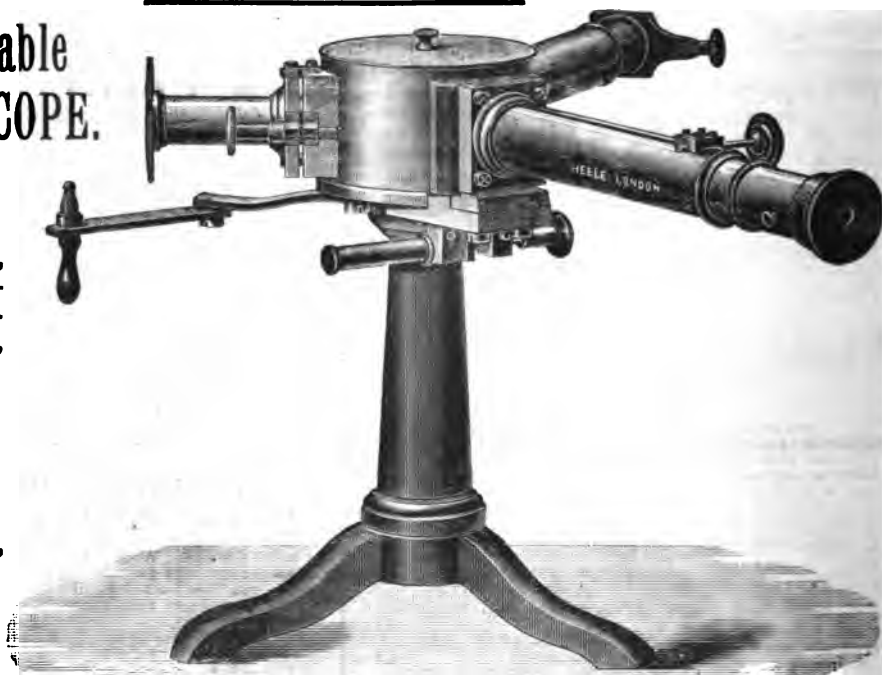
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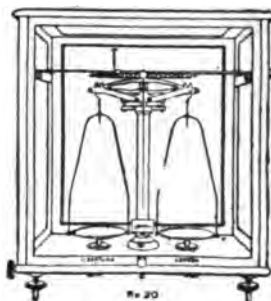
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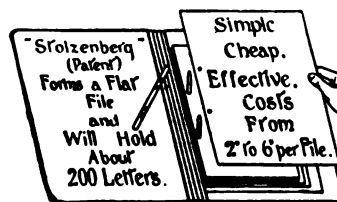
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THE CHEMICAL NEWS.

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THORIANITE, A NEW MINERAL FROM CEYLON.*

By WYNDHAM R. DUNSTAN, M.A., LL.D., F.R.S.,
and
G. S. BLAKE, A.R.S.M.,
Assistant in the Scientific and Technical Department of the
Imperial Institute.

THE mineral which forms the subject of this paper was collected in Ceylon during the progress of the mineral survey of the island, which was commenced in 1903, under Professor Dunstan's supervision, with the principal object of determining the extent to which economic minerals, such as graphite, mica, &c. occur, and if possible of discovering other minerals of commercial importance. The minerals collected by Mr. A. K. Coomaraswamy and Mr. James Parsons, the officers entrusted with the survey in Ceylon, are submitted to examination and analysis in the Scientific and Technical Department of the Imperial Institute, and are subsequently subjected to such technical trials as may be necessary in order to ascertain their precise uses and to determine their value.

Among the materials thus received from Ceylon at the Imperial Institute was a small quantity of a heavy black mineral occurring chiefly in small roughly cubical crystals. This mineral was, in the first instance, furnished to the officers of the mineral survey by Mr. W. D. Holland, who believed it to be uraninite or pitchblende. He had previously sent specimens to several persons in this country under this name.

A chemical examination of the small specimen received at the Imperial Institute showed, however, that the mineral contained a large proportion of thorium in the form of the dioxide (thoria) and only a small proportion of uranium. It was evident that this was a new mineral chiefly composed of uncombined thoria (ThO_2). Pending the arrival of more material to enable a further examination of its properties to be made, a preliminary account of its composition and properties was communicated by one of us to *Nature* (March 30, 1904, p. 510), and the name *thorianite* was suggested for the substance, which contained at least 75 per cent of thoria.

It was also stated that the mineral was radio-active and that it apparently contained helium, points which would be made the subject of further investigation.

The publication of these results was followed by a communication to *Nature* (April 7, 1904, p. 533), from Sir W. Ramsay, who announced that he had purchased 6 cwt. of the mineral from Mr. Holland some months previously and had been engaged in its examination. He was unable to confirm the statement that it contained thoria, but announced that it had furnished considerable quantities of helium. In a second communication to *Nature* (April 14, 1904, p. 559), Sir W. Ramsay modified the statement he had previously made that the mineral contained practically no thorium.

Further small supplies of the mineral having since been received at the Imperial Institute, we have been enabled to confirm the conclusion first arrived at that the substance is chiefly composed of thoria, and we now desire to bring before the Royal Society an account of this remarkable new mineral, for which the name *thorianite* is appropriate.

A general account of the composition, properties, and uses of *thorianite* is included in Professor Dunstan's official "Reports on the Results of the Mineral Survey in Ceylon, 1903-4," which was issued as a Parliamentary Paper (Cd 2341) in January, 1905.

Occurrence of Thorianite in Ceylon.

The following account of the occurrence of the mineral, at first supposed to be "uraninite," has been given in official reports by Mr. A. K. Coomaraswamy, B.Sc., the Director of the Mineral Survey in Ceylon.

"Mr. Holland of Dikmukulana has for long taken an interest in local mineralogy, amongst other things obtaining specimens of 'nampu' (gem-bearing gravels) from as many localities as possible by offering a small reward to the native 'gemmers' who bring it. It is difficult to persuade the native that gems are not required or to get him to reveal the true source of 'nampu.' These difficulties overcome, the examination of 'nampus' is an ideal method of gaining a knowledge of heavy minerals of any district. Early in 1903 Mr. Holland obtained 'uraninite' amongst his samples and was gradually able to get as much as 6 cwt. brought to him along with other stuff. This material was sent to England and sold to Sir W. Ramsay at the rate of £50 for 6 cwt. Subsequently Mr. Holland induced a native to show him the source of the material, and finding that some quantity occurred, he took out a prospecting license in the full belief that the locality was Crown land.

"Thorianite, together with a mineral regarded as thorite, and a number of other heavy minerals, is found near Kondurugala, Bambarabotuwa, Province of Sabaragamuwa. The principal deposit occurs in and near the bed of the upper part of the Kuda Pandi-oia, a small stream, which at first occupying a small north-west and south-east strike valley north of the Hopewell-Hapugastenna bridge path, turns through nearly a right angle and joins the Maha Pandi-oia a little below the same path. In the bed of the Kuda Pandi-oia, and in a small 'deniya' swamp just below the swamp, the thorianite is to be obtained in considerable abundance. It could not be discovered *in situ*, but it can hardly be doubted that it is derived from some rock outcropping not far distant from the highest part of the little stream; the stream is so small that after a few days of drought (not very usual in this wet district) no running water is met with above the camp. The matrix is no doubt a rock of granitic type similar to those containing zircon, allanite, &c., which have been met with elsewhere in the Balangoda district, intrusive in the Char-nockite series, and classed as belonging to the Balangoda group. Of these rocks the largest exposure (a narrow lenticular mass two miles or more in length) is that of zircon granite on Massena estate (six miles);* the rock consists of feldspars, quartz, biotite, zircon, and ilmenite; smaller exposures of zircon granite are found on Herimitigala (eight miles) and Hopewell estates (15 miles); at Denegama bridge, on the road between Balangoda and Belihul-oia, and near the 91st milepost on the same road. There are also similar granites without accessory minerals exposed—e.g., on the main road about a mile below Balangoda. The allanite-granite, or pegmatite, is best seen on Lower Denegama estate, where it occurs as a dyke 3 or 4 feet thick, forming a conspicuous ledge in the bed of the stream which runs through that part of the estate. The rock is composed of feldspars (chiefly orthoclase), quartz, biotite, and allanite. The allanite forms thin tubular idiomorphic and larger irregular crystals, the biggest having a greatest diameter of 3 inches. Almost identical rocks occur (1) in the Weweldola on Dikmukulana estate (11 miles), and (2) at Weligepola (9 miles). It is important to observe that a pegmatite rock, composed mainly of pink orthoclase, quartz, and biotite, with accessory apatite, tourmaline, ilmenite, &c., has been observed on Ambalawa estate, Gampola ("Spolia Zeylanica," vol. i., part 4, 1904), containing, in addition to the above-named minerals, a few cubic crystals of a black mineral at first regarded as uraninite, but which is almost certainly thorianite.

"To return to the Kondurugala locality, the thorianite is probably derived from a granitic rock with no very large

* A Paper read before the Royal Society, May 18, 1905.

* The distances are quoted from Balangoda.

outcrop, but in which it occurs in considerable abundance; perhaps together with the zircon, thorite, and ilmenite, which quite possibly, however, occur separately in other rocks of a similar character. The outcrop of this rock could not be discovered owing to the dense jungle and thick soil and landslips; rock (mainly decomposed granite) is indeed exposed at several points in the beds of the Kuda Pandi-oya and of the small streams joining it, but any search for the outcrop of a particular rock in the adjoining jungle could only be expected to succeed at the cost of a large expenditure of time and money, and might even then result in failure.

"There is a large area, including at least the whole of Sabaragamuwa and parts of the central, western, and southern provinces, wherein this or other rare heavy minerals may be looked for.

"It is unlikely that any very extensive deposit of any of these rare heavy minerals will be found, but they may be expected to occur at various points in moderate amounts. In the Kuda Pandi-oya valley a total of 5 tons might, perhaps, be obtained; from the Alupola-dola or the Kuda-oya I doubt if half a ton could be profitably extracted, but these estimates are quite uncertain. The Gampola occurrence is quite without commercial value. The total amount actually obtained in Bambarabotuwa, so far, does not exceed 15 cwts. In the immediate neighbourhood of Kondurugala the Walaweduwa jungle seems the most favourable district for investigation. An examination of the Ratganga valley towards the west showed that thorianite is absent there, and that even zircon is very scarce; but on the north-east one or two heavy minerals not yet determined were actually obtained in the southern part of the Walaweduwa Crown Forest Reserve, and further work on that side of Kondurugala might be useful. It must be mentioned, however, that the district is a very wet one, the jungles swarming with leeches; it is also very inaccessible, provisions and camping effects having to be carried fully 20 miles from Balangoda. Camping in these jungles is absolutely useless except in fine weather; and in the absence of a detailed map observations cannot be very accurately set down.

"Since August, 1904, a small deposit of the mineral provisionally identified as thorite was discovered at Durayakanda, South of Gilimale, about six miles from Ratnapura.

"A further amount of 1200 lbs. of thorianite has since been obtained from Bambarabotuwa."

Description of Thorianite.

Thorianite, as it occurs naturally, is often associated with other minerals, and is not easy to obtain in a completely separate condition.

Dr. J. W. Evans has made a preliminary examination of the crystallographic characters, and intends to further study this subject. It may be stated now that the mineral occurs in small cube-like crystals up to nearly a centimetre in diameter, the largest so far seen measuring rather more than 8 m.m. In most specimens the colour is a dull grey or slightly brownish black, but those crystals which have not suffered from attrition in the streams are a jet black with a bright resinous or pitchy lustre. The difference may be attributed partly to the grinding of the surface and partly to superficial chemical changes. The mineral thus differs from uraninite or pitchblende, which usually occurs massive, and not obviously crystalline. The streak furnished by uraninite is brown with a tinge of green.

By transmitted light the mineral is opaque except in thin sections.

The double refraction is very low. The refractive index probably exceeds 1.8.

The only faces that are ordinarily developed on the crystals of thorianite are apparently those of the cube. These have a very uneven surface, especially in specimens that have not suffered much from attrition or alteration. This character of the surface is mainly the result of the

development of a number of small vicinal faces. In some cases larger faces of similar character are present, meeting at very obtuse re-entrant or salient angles, and reminding one of those seen in some crystals of fluorspar. In other crystals the faces show a more or less irregular curvature.

The indefinite character of the surface prevents any accurate determination of the angles. The goniometric readings vary 2 or 3 degrees on either side of 90 degrees, according to the portions of the surface from which the image is reflected, but there is in most cases no satisfactory evidence that the faces as a whole are not virtually at right angles. Some crystals, however, appear to be distorted and have angles differing from a right angle by as much as 5 degrees or even more.

Occasionally twin crystals are met with, and these are of some interest. They are interpenetrant twins on a face of the octahedron as twinning plane, and one of the diagonals of the cube as twinning axis, exactly similar to those of fluorspar. As in the case of that mineral the coigns of one cube project as pyramids on an isosceles triangular base on the face of the other. Sometimes the compound form is almost completely regular, four edges of each cube meeting at one point or approximately so at both ends of the common diagonal that forms the twinning axis; at other times the composition is more irregular, and a number of coigns project from the faces of a cube in such a manner that, though the faces of one coign are parallel to those of another, they are not in the same plane. In these forms the twinning axis and plane are the same for all the coigns, even when there is more than one projecting from the same face, the more acute point of the pyramid pointing to the coign of the cube from which the twinning axis emerges. The diagonal which constitutes this axis has therefore crystallographic characters different from those of the other three diagonals, about which this twinning cannot apparently take place, and the symmetry of the crystal must be considered as rather rhombohedral than cubic, although the angles are apparently right angles. The same considerations would apply to fluorspar, in which case the essentially rhombohedral character of its symmetry is confirmed by the occurrence of crystals in which only those faces of the four faced cube or tetrakis hexahedron {310} are developed, in which the finite intercepts are of opposite signs. These faces may be represented by the symbol {310}, and are those which bevel the edges that do not pass through the coigns at the ends of the unique diagonal. They together form a scalenohedron, which is in fact the scalenohedron {1342} of the rhombohedral system, assuming the cube as the fundamental rhombohedron. ("Lehrbuch der reinen und Angewandten Krystallographie," 1830, p. 178, Fig. 572).

A similar scalenohedron {210} or {1231} is repeatedly met with in crystals of halite. (F. von Kobell, "Über Merkwürdige Krystalle von Steinsalz," *Journ. für Prakt. Chemie*, 1861, vol. lxxxiv., p. 420; K. André, "Über Steinsalz Krystalle von hexagonal-rhomboëdrischer Pseudosymmetrie aus Sicilien," *Centralb. für Mineralogie*, 1904, p. 88).

It is interesting to notice that chabazite, which is cubic in general appearance, but really rhombohedral, having its angles differing from right angles by nearly 5 degrees, twins in exactly the same manner as fluorspar and thorianite.

The inference that thorianite is essentially rhombohedral in character is confirmed by the observation that in sections cut perpendicular to the twinning axis the substance is practically isotropic.

Thorianite shows no definite cleavage, but the mineral is traversed by irregular cracks which appear to follow the direction of the basal plane more frequently than any other. On fracture, it shows an irregular surface, which is more or less conchoidal on a small scale.

The hardness of the mineral is nearly 7, which distinguishes it at once from uraninite with a hardness of 5.5.

Under the blowpipe thorianite is infusible. It decrepitates, and if raised to a sufficiently high temperature is highly incandescent.

It is sometimes associated in rolled fragments with a smooth, yellow-brown, apparently amorphous material, of hardness 6, which envelopes it or forms a rounded deposit on its faces. This substance is reddish-yellow in colour when viewed in thin sections by transmitted light. Zircon also sometimes occurs intergrown with thorianite.

The density of different specimens of thorianite varies between 8 to 9.5 and 9.7. The higher numbers probably represent the density of the actual mineral, which in some cases exhibits cavities partially filled with a yellow ochreous material and also inclusions of zircon, one of the minerals generally associated with thorianite, and these associated minerals, especially those which contain thorium, will be investigated if a sufficient quantity can be obtained separated from thorianite.

The mineral is easily powdered and then dissolves readily in strong nitric acid or in diluted sulphuric acid, with evolution of a gas which is chiefly helium. Thorianite is scarcely attacked by hydrochloric acid.

Thorianite is highly radio-active, and, in fact, may prove to be one of the most radio-active of minerals. The cause of this radio-activity is referred to below.

(To be continued).

THE COMPLETE ANALYSIS OF LEAD ORES.

By J. A. MULLER.

I. The method of estimating lead in galena, first proposed by F. Stolba and improved by Fr. Mohr ("Fresenius," 6th French edition, p. 975), has not given me satisfactory results. The determination of lead in its ores can be effected much more accurately by weighing this element in the state of sulphide, as has been shown in a previous paper.

The following is the best method, according to experiments I have made on this subject, for estimating the lead and also the other elements and compounds which accompany lead in its ores.

To about 1.5 grms. of the finely powdered ore, weighed accurately in a covered platinum crucible, we add gradually 10 c.c. of nitric acid (density = 1.33) and leave the mixture in a warm place for twelve hours. Exhaust the residue—from which the greater portion of the excess of acid is removed—in the same crucible with warm water, and filter through a small filter. Without troubling whether the filtrate is a little cloudy or not, we add 40 c.c. of a 10 per cent solution of acetate of soda, bring the mixture to boiling, and filter to separate the ferruginous precipitate.

In the filtrate the silver is precipitated by a slight excess of hydrochloric acid. As for the ferruginous precipitate, it is dissolved in hydrochloric acid, and the solution added to the product of exhaustion, at about 80°, of the residue insoluble in water, by about 60 c.c. of a mixture of equal volumes of fuming hydrochloric acid and water. After washing with boiling water we add to the clear filtrate that resulting from the filtration of the AgCl, and enough water to make 1.5 litres of liquid, which is heated to about 70°, and saturated with H₂S, then let stand for a day, and filtered.

The portion insoluble in hydrochloric acid contains the quartz, the insoluble silicates, and the greater part of the sulphate of baryta. After calcination and weighing, we can estimate the silica by difference by treating with hydrofluoric acid.

As for the precipitate formed by sulphuretted hydrogen, it is filtered on a tared filter, washed, and detached as completely as possible from the filter, and the aqueous magma, containing about 50 c.c. of water, treated with 6 c.c. of a concentrated solution of sulphurised ammonium sulphide (or, in the presence of copper, with sulphurised sulphide of sodium), at a temperature below boiling; the liquid is decanted on to a tared filter-paper, and the residue again treated three or four times, hot, with a small quantity

of water containing 0.5 c.c. of the sulphurised sulphide; finally, we wash with pure water, and, after having changed the recipient, with alcohol, &c., the precipitate is dried *in vacuo* over sulphuric acid, and weighed.

The precipitate of sulphide of lead may contain cupric sulphide and also a small quantity of sulphide of silver. This latter metal is estimated by treating an aliquot part of the precipitate with iron at a red heat in the presence of an alkali, and submitting the metallic button obtained to cupellation. Traces of gold may be also looked for by cupellation, but the ore itself must be used. Take up the small globule of silver with nitric acid, and the gold remains as residue. As for the copper, if present, it must be separated from the lead by transforming an aliquot part of the precipitate of sulphide into sulphate by means of nitric acid, then after the addition of a little sulphuric acid and a drop of hydrochloric, separate the soluble sulphate of copper in a mixture of alcohol and water.

The sulphurous solution already obtained contains arsenic and antimony; it is acidulated slightly with hydrochloric acid, then filtered immediately, and the precipitate washed with water, alcohol, &c.; the precipitate almost free from sulphur is then dried, and treated at boiling temperature with a mixture of two volumes of fuming hydrochloric acid and one volume of water (about 60 c.c. altogether). In the dilute hydrochloric solution the antimony is precipitated in the form of sulphide, and then estimated as such.

As for the insoluble sulphide of arsenic, mixed with a little sulphur, it is dissolved in boiling nitric acid (density = 1.33) and the arsenic estimated in the form of ammonio-magnesian arseniate (AsO₄NH₄Mg + 0.5H₂O at 102°). It is necessary to re-dissolve the precipitated arseniate and to re-precipitate it, adding only a small quantity of magnesian mixture. In the mother-liquors from the precipitates of arseniate there are still small quantities of arsenic and antimony, which may be precipitated by H₂S in acid solution, and separated as described above.

The liquid separated by filtration from the precipitated PbS, &c., may still contain iron, zinc, and calcium. The sulphuretted hydrogen is driven off by boiling, and the solution is then concentrated down to one-third of its volume; it is oxidised by means of bromine, and made alkaline with ammonia; the precipitate of Fe₂O₃ formed should be re-dissolved in the smallest possible quantity of hydrochloric acid to separate from it the sulphate of baryta which may be present, then the solution is re-precipitated by ammonia in the presence of a little chloride of ammonium. The zinc is estimated in the form of sulphide, and the calcium as oxide after precipitation as oxalate. After the separation of this latter metal the filtered liquid is evaporated to dryness, the residue is calcined and taken up with a little dilute hydrochloric acid to separate a further possible quantity of sulphate of barium.

II. The bodies generally accompanying galena in its ores are, besides the products of the decomposition of the sulphide of lead—such as anglesite and cerussite—quartz and silicates, blende, calcite, fluorite, barytine, and pyrites; finally, in certain varieties we also meet with arsenic and antimony. Argentiferous galenas contain from 0.01 to 1.0 per cent of silver.

For the purpose of checking the method of analysis just described, I made an intimate mixture of the following porphyrised compounds:—Crystals of pyrites (without copper and with 46.44 per cent Fe), 0.685 gm.; pure fluorine, 1.195 grms.; pure quartz, 0.649 gm.; pure crystallised sulphate of baryta, 3.217 grms.; pure crystallised carbonate of lime, 0.313 gm.; sulphide of zinc at 97 per cent sulphur, 0.714 gm.; pure sulphide of arsenic, 0.188 gm.; pure sulphide of antimony, 0.276 gm.; sulphide of silver precipitated and dried *in vacuo*, 0.337 gm. The six latter bodies were obtained artificially.

Two assays, A and B, were made; in the former we analysed a mixture composed of 0.5956 gm. PbS at 0.15 per cent of water and 0.6122 gm. of the above mixture; in the latter the sample analysed consisted of 0.7034 gm.

of the same sulphide of lead and 0.6073 grm. of the preceding mixture.

The following results were obtained:—

	Assay A.		Assay B.	
	Calculated. Grm.	Found. Grm.	Calculated. Grm.	Found. Grm.
Pb ..	0.5148	0.5197	0.6081	0.6135
Ca ..	0.0597	0.0606	0.0592	0.0590
Zn ..	0.0376	0.0370	0.0373	0.0372
Fe ..	0.0257	0.0281	0.0255	0.0285
As ..	0.0093	0.0075	0.0092	0.0085
Sb ..	0.0159	0.0146	0.0158	0.0154
Ag ..	0.0237	0.0203	0.0235	0.0224
LiO ₂ ..	0.0525	0.0514	0.0520	0.0498
BaSO ₄ ..	0.2600	0.2631	0.2579	0.2525

—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 24.

THE ESTIMATION OF PHOSPHORIC ACID IN FOODS.

By E. FLEURENT.

THE total quantity of phosphorus entering into the composition of the animal and vegetable materials constituting our food is an important factor in the alimentary value of these products. Up to quite recently the determination of this element was effected by starting with the ashes obtained by the incineration of a known weight of the material in question, either with or without a certain quantity of caustic lime, and finally estimating the pyrophosphate of magnesia obtained by the calcination of the precipitated ammonio-magnesian phosphate. M. Garola ("International Congress of Applied Chemistry, 1896," vol. ii., p. 161) has shown by means of experiments with wheat, that the operation carried out in this manner leads to the loss of a considerable proportion of the phosphorus (31 per cent of the amount estimated) on account of the reduction of the acid phosphates by the carbon of the organic matter,* and he proposed to use Kjeldahl's method for the destruction of this latter substance, as generally used in laboratories. In practice the destruction of the organic matter by this method is very long, and therefore it becomes necessary to operate only on small samples, say, for 2 to 4 grms.

We next meet with the following drawback:—The phosphorus being only a very small part of the substance to be examined, the precipitation in the form of ammonio-magnesian phosphate is no longer convenient, as it leaves as the residue in the final calcination an amount of pyrophosphate too small to be used with safety in the calculation of the percentage present. M. Garola has got round this difficulty by precipitating the phosphoric acid with molybdate of ammonia, and weighing, with certain precautions which he points out, the phospho-molybdate obtained, and then calculating the phosphoric acid by means of the coefficient 3.54, the invariability of which he has made certain of under the conditions of the experiment.

The method devised by M. Garola leads to exact results provided it is followed with the greatest care in all its details. It sometimes happens, however, as I have found in practice, that in spite of all the attention that may be given to the operation the invariability of the coefficient 3.54 is not always certain, so that there is this objection to the method, that this variability of the coefficient and the small amount of the sample taken may lead finally to an important multiplication of the errors inherent to all analytical methods.

To avoid these various drawbacks, I have for some years past used a method in my own laboratory which, based on the destruction of the organic matter by the successive

* In a research I am now carrying on in my laboratory I am going on to the mechanism of this loss.

use of nitric and sulphuric acids, enables me to work on 10 or 20 grms. of material, according to its richness in phosphorus, and thus in every case to weigh a proportion of pyrophosphate of magnesia always sufficient to ensure the correctness of the analytical calculations.

The following is the manner in which this method must be applied:—If the material contains an excessive proportion of moisture it is previously dried and reduced to powder; if not, it is used in the condition it happens to be in, in a state of division suitable for the attack. We then weigh 10 or 20 grms. which are placed in a conical flask of 300 c.c. capacity, and covered with 50 to 100 c.c. of fuming nitric acid of 1.48 density. We heat carefully at first, gently agitating the flask with a circular movement, so as to break down the froth which is formed by the abundant disengagement of gas, and to prevent the mass running over. We then continue the evaporation until only a few m.m. of liquid remain at the bottom of the flask, and finally complete the evaporation to dryness in the oven at 110 to 120°. On this residue we pour 15 to 20 c.c. of sulphuric acid (two-thirds acid at 66°, and one-third fuming acid), add one drop of mercury, and finish the attack in the manner described by Kjeldahl.

The attack finished, we dilute carefully with distilled water, and saturate the sulphuric acid with ammonia, taking care to keep the mixture cool. Transfer to a precipitating glass, using the following mixture as wash-water:—Ammonia, 500 c.c.; NH₄Cl, 200 c.c.; water to 1 litre.

We then precipitate with magnesia mixture, and complete the estimation in the ordinary manner.

The following figures, obtained in duplicate on various animal and vegetable food materials, show the sensitiveness of the method and the concordance it is possible to obtain:—

	Moisture.	P ₂ O ₅ per cent on the dry material.	
		I.	II.
Haricot flour	18.14	1.077	1.079
Camembert cheese	46.96	1.102	1.105
Yolk of egg	49.06	2.843	2.845
Lean beef	74.00	1.894	1.904
Brie cheese	53.24	1.272	1.273
Gruyère cheese	35.15	2.475	2.495
Wheat-flour (70 per cent extraction)	15.46	0.357	0.344
Cabbage leaves	89.00	1.625	1.621

—*Bull. Soc. Chim.*, Series 3, vol. xxxiii., No. 1.

THE CONSTITUTION OF THE HYDROSULPHITES.

By MAURICE PRUD'HOMME.

A SEALED packet was deposited by Em. Zundel, manufacturer of muslins, of Moscow, at the Société Industrielle de Mulhouse, on December 15, 1902. It describes the interesting observation that the hydrosulphites unite with formic aldehyde, giving crystallisable double compounds, analogous with those formed by the bisulphites with the aldehydes. These bodies are much more stable than the simple hydrosulphites, even than the slightly soluble hydrosulphites, such as that of zinc. It is only under the action of steam at 100° that the double hydrosulphite of soda-formaldehyde, for example, splits up into formic aldehyde and hydrosulphite of soda, which, in the nascent state, acts as a reducing agent of uncommon energy.

The chemists belonging to the firm of Em. Zundel, Messrs. Schwartz, Baumann, Sunder, and Thesmar, have utilised the properties of the bodies discovered by them for the direct fixation of indigo, and for the production of perfect white prints on tissues tinted with insoluble azoic colouring materials, such as paranitraniline red, *n*-naphthylamine garnet, &c.

Quite recently Messrs. Baumann, Thesmar, and Frossard presented to the Société Industrielle de Mulhouse (Nov. 9, 1904) a paper on the constitution of formaldehyde hydrosulphite, of which we will discuss the essential points.

Hydrosulphite of soda is prepared from bisulphite of soda, sulphuric acid, and zinc in the presence of ice. When the reaction is completed the whole of the zinc is precipitated by means of Solvay's soda, sifted into the liquor. When the latter is neutral it is passed to the filter-press, and precipitated with sea-salt. The precipitate is filtered, pressed strongly, and mixed with the necessary quantity of formaldehyde at 40 per cent.

On cooling, the liquor gave an abundant crystallisation of what seemed to be a well-defined product. Nevertheless, by means of fractional crystallisations in dilute alcohol, we are able to divide it into two bodies, one of which is the bisulphite of soda-formaldehyde, $\text{SO}_3\text{NaH} + \text{CH}_2\text{O} + \text{H}_2\text{O}$, and the other the bihydrosulphite of soda-formaldehyde, $\text{SO}_2\text{NaH} + \text{CH}_2\text{O} + 2\text{H}_2\text{O}$, which occurs in the form of magnificent crystals, apparently belonging to the clinorhombic system.

Messrs. A. Bernthsen and M. Bazlen in a recent paper (*Berichte*, 1900, vol. xxxiii., p. 126; and *Bull. Soc. Chim.*, 1900, [3], vol. xxiv., p. 404) on hydrosulphite of soda, prepared by means of a mixture of bisulphite of soda, sulphurous acid, and zinc, and precipitated by sea-salt, deduced from their analyses the constitutional formula $\text{S}_2\text{O}_4\text{Na}_2 + 2\text{H}_2\text{O}$ for hydrosulphite of soda, and explained its formation by the equation—



We know, on the other hand, that Schutzenberger has always upheld the formula SO_2NaH for hydrosulphite of soda. This is now absolutely confirmed by the work of the Moscow chemists, who have definitely established that M. Bernthsen's salt is not, as he supposed, the neutral hydrosulphite of soda in a state of purity, but a mixture of 1 molecule of bisulphite of soda and 1 molecule of the true acid hydrosulphite discovered and described by Schutzenberger.

With the work of Messrs. Baumann, Thesmar, and Frossard is connected directly the beautiful experiment of Moissan (*Bull. Soc. Chim.*, 1903, [3], vol. xxix., p. 10) on the reciprocal action of the alkaline or alkaline-earthly hydrides and sulphurous anhydride, which may be formulated $2\text{KH} + 2\text{SO}_2 = \text{S}_2\text{O}_4\text{K}_2 + \text{H}_2$.

The white salt thus obtained, taken up with a small quantity of water free from oxygen, gives, by simple evaporation away from the air, fine transparent needles or small acicular crystals grouped together in stars, and gives the characteristic reducing reactions of the alkaline hydrosulphites.

The salt, $\text{S}_2\text{O}_4\text{K}_2$, thus hydrolyses in contact with water; one of the terms of the reaction being the bihydrosulphite, which we know has for its formula SO_2KH , the other must necessarily be bisulphite of potassium according to the equation $\text{S}_2\text{O}_4\text{K}_2 + \text{H}_2\text{O} = \text{SO}_2\text{KH} + \text{SO}_3\text{KH}$. This fact agrees with the formation of two distinct crystalline forms.

M. Bernthsen's salt, $\text{S}_2\text{O}_4\text{Na}_2 + 2\text{H}_2\text{O}$, admitting its existence as a chemical body, would be a hydrate of M. Moissan's corresponding salt, $\text{S}_2\text{O}_4\text{Na}_2$. As it is isolated by precipitation with sea-salt, the contact with the saline solution might very well bring about hydrolysis, and cause the formation of a body with a certain stability. But in the presence of pure water it should be hydrolysed like M. Moissan's salt, and decomposed into its elements. If we react with zinc on its aqueous solution, the free bisulphite should then give rise to a further quantity of bihydrosulphite.

Titration with iodine, with or without carbonate of soda, as described by the Moscow chemists, would enable us to make certain of the progress of the reaction and to observe the action of the hydrolysis.

The crystalline bodies of the type $\text{S}_2\text{O}_4\text{M}_2$, obtained by

M. Moissan by the dry way, do not raise the same doubts as the compound $\text{S}_2\text{O}_4\text{Na}_2 + 2\text{H}_2\text{O}$ of M. Bernthsen, and should be looked upon as the neutral salts of a new sulphuric acid, $\text{S}_2\text{O}_4\text{H}_2$.—*Bull. Soc. Chim.*, Series 3, vol. xxxiii., No. 2.

MEETING OF THE BRITISH ASSOCIATION IN SOUTH AFRICA.

THE arrangements for the forthcoming meeting of the British Association in South Africa have now been completed, and Mr. Silva White, the Assistant Secretary of the Association, sailed for Cape Town in the *Walmer Castle* on Saturday, July 1. The number of members who will proceed to South Africa to attend the meeting is 385, and of these no less than 276 members have intimated their intention to visit the Victoria Falls at the conclusion of the ordinary work of the Association. The official party, consisting of leading representatives of Science and guests of the Association, with the General and Sectional Officers for this meeting and the President, numbers 140 in all, and will sail by the *Saxon* on July 29. Most of the other members will proceed to the meeting by the *Durham Castle* and the *Kildonan Castle*, both of which sail on July 22.

In a previous article (*CHEMICAL NEWS*, xci., p. 52) the local arrangements for the meeting were described. There will be receptions and social functions, excursions, &c., at Cape Town, Durban, Pietermaritzburg, Johannesburg, Kimberley, and Bulawayo. The Central Organising Committee for South Africa (chairman, Sir David Gill, K.C.B., F.R.S.; hon. secretary, Dr. Gilchrist) has carried out the co-ordinating work of the programme. The lists of local committees and sub-committees contain nearly one thousand names, from which it may be concluded that much interest is taken in the meeting.

As already mentioned, lectures of a popular character will be delivered at the chief towns visited. These lectures have now been definitely arranged as follows:—

Cape Town.—W. J. Burchell's discoveries in South Africa, Prof. Poulton; some surface actions of fluids, Mr. C. V. Boys.

Durban.—Mountains: the highest Himalaya, Mr. D. Freshfield.

Pietermaritzburg.—Sleeping-sickness, Colonel D. Bruce; *Johannesburg*.—Distribution of power, Prof. Ayrton; steel as an igneous rock, Prof. Arnold.

Pretoria.—Fly-borne diseases, malaria, sleeping-sickness, &c., Mr. A. E. Shipley.

Bloemfontein.—The Milky Way and the clouds of Magellan, Mr. A. R. Hinks.

Kimberley.—Diamonds, Sir William Crookes; bearing of engineering on mining, Prof. Porter.

Bulawayo.—Zimbabwe, Mr. Randall MacIver.

The President's Address to the Association will be delivered at Cape Town on August 15, and at Johannesburg on August 30. Mr. G. W. Lamplugh's report on the geology of the Victoria Falls will take the form of an afternoon Address to Section C at Johannesburg.

Subjoined is a draft programme of the work of the sections:—

Section A (Mathematics and Physics).—*Cape Town*: President's address; progress of the arc of meridian and geodetic survey of South Africa, Sir D. Gill; to what extent can the ether affect the motion of matter? Prof. J. Larmor; observations of atmospheric electricity in South Africa, Prof. Beattie and Mr. Lyle; leak of electricity from certain heated substances, Prof. Beattie; the foundations of the kinetic theory of gases, Mr. Burbury; application of the kinetic theory of nebulae, Mr. J. H. Jeans; radiation at low temperatures, Dr. J. T. Bottomley. There will also probably be communications from Mr. Hough on tides, and from Dr. Roberts on the Algal variables

Johannesburg: On the teaching of elementary mechanics (jointly with Section L if possible), Prof. J. Perry; on flight, Prof. G. H. Bryan; (1) electrical conductivity in relation to chemical action; (2) magnetic survey of South Africa, Prof. Beattie; report of the seismological committee, Prof. J. Milne; a form of dry Daniel cell, Mr. J. Brown; the strength of winding ropes in mines, Prof. Perry; the experimental foundations of the theory of heat conduction, Dr. C. H. Lees. There will probably be a communication from Mr. Sutton on the meteorology of South Africa.

Section B (Chemistry).—Detailed information regarding papers offered by members in South Africa has not yet been received, but the following provisional arrangement has been made:—**Cape Town**: Recent advances in agricultural science, A. D. Hall; vegetable assimilation, Dr. Horace T. Brown; enzyme action, Dr. E. F. Armstrong. These communications are intended to serve as a basis of discussion of agricultural chemical problems. **Johannesburg**: President's address; reports on various aspects of the metallurgy of gold by local experts. Communications by Dr. H. Marshall on the experimental basis of the dissociation hypothesis, and by H. Ingle on the soils of the Transvaal, have been provisionally accepted.

Section C (Geology).—**Cape Town**: Opening remarks by the President; the continent of Africa in relation to the physical history of the earth, Prof. W. J. Sollas; the classification of the Karroo beds of South Africa, Prof. R. Broom; report of the committee on the fauna and flora of the English Trias, J. Lomas; extraordinary daily fluctuations in a Karroo well, Prof. A. Young; and other papers on the Karroo or Trias. **Joint meeting with Section E (Geography).**—The physical geography of Cape Colony, H. C. Schunke-Holloway; Glacial periods in South Africa, A. W. Rogers; changes of climate as shown by movements of the snow line and upper tree line since Tertiary times, Prof. A. Penck; physiographical subject, Prof. W. M. Davis; Bavarian's Kloof, a contribution to the theory of mountain folds, E. H. L. Schwarz; the Stormberg formation in the Cape Colony, A. L. Du Toit; on the geology of South Victoria Land, H. T. Ferrar. **Johannesburg**: President's address; magnetic segregation of sulphide ores, Dr. A. P. Coleman; marginal phenomena of granite domes, Prof. G. A. J. Cole; relation of the igneous rocks to the crystalline schists, F. P. Mennell; the indicators of the goldfield of Ballarat, Prof. J. W. Gregory; petrographical subject, Prof. R. B. Young; the diamond pipes and fissures of South Africa, H. S. Harger; recent work of the Transvaal Geological Survey, H. Kynaston; the Victoria Falls, G. W. Lamplugh; the great laccolitic intrusions of the Bushveld, Dr. G. A. F. Molengraaff; evidences in the Transvaal of Glacial conditions in permo-Carboniferous times, E. T. Mellor; geological notes on the excursion to Pretoria, A. L. Hall; the great West Rand upthrust, Dr. J. T. Carrick; notes on a sedimentary formation older than the Witwatersrand beds, E. Jorissen; interesting outlines of the Witwatersrand formation, Dr. J. T. Carrick.

Section D (Zoology).—**Cape Town**: President's address; the Triassic reptiles of South Africa, with remarks on the origin of mammals, Dr. Broom; a comparison of the Permian reptiles of Russia with those of South Africa, Prof. Amalitzky; South African scorpions, Dr. Purcell; recent work on gametogenesis and its bearing on theories of heredity, L. Doncaster; the migration of birds, in the southern hemisphere, W. L. Sclater; the ostrich, A. H. Evans. **Johannesburg**: Pearl oysters and pearls, Prof. Herdman; recent discoveries in the South African deep sea, Dr. Gilchrist; cephalopodiscus, Dr. Harmer; the growing-point in vertebrates, Prof. Cleland; South African ticks, Drs. Cooper-Foster and Nuttall.

Section E (Geography).—**Cape Town**: President's address; afforestation of South Africa; the unveiling of the coasts of Africa (lantern views of old maps), H. Yule Oldham; the Ordnance Survey of the United Kingdom, Colonel Johnston; a comparison of the periodicity of the

meteorological conditions of London and Cape Town, Dr. H. R. Mill; Gough Island, Rudmose Brown; terrestrial globes as a necessary adjunct to the teaching of geography, Captain Creak; excursions as a means of teaching geography (lantern), J. Lomas. **Johannesburg**: The evolution of Africa, Dr. J. Scott Keltie; a new rainfall map of Africa, A. J. Herbertson and P. C. Waite; boundaries and areas in Africa, J. Bolton; the physical geography of the Transvaal, Tudor Trevor; notes on the geography of Africa south of the Limpopo, F. S. Watermeyer; the game preserves of the Transvaal, Major Stevenson Hamilton, D.S.O.; the Sikhim, Himalayas, and Tibet, Douglas W. Freshfield; Asiatic subject, Prof. Cordier.

Section G (Engineering).—**Cape Town**: Metcalf on Zambezi Bridge and Rhodesian Railways; ocean turbine boats, Prof. Byles; roller bearings, wire ropes in mines, and probably automobiles. **Johannesburg**: President's address (irrigation); strength of winding ropes in mines, Prof. Perry.

Section H (Anthropology).—**Cape Town**: President's address; the totemism of the Bantu, E. S. Hartland; the musical instruments of the natives of South Africa, Hy. Balfour; American negroes, Miss Pullen-Burry; artificial deformation in Africa, Dr. von Luchan. **Johannesburg**: arts and crafts among the natives of South Africa, Dr. Shoenland; stone implements in South Africa, Mr. Johnstone; bushman paintings with reproductions, Dr. Squire; the affinities of the Hottentots, Dr. von Luchan; the Modjadje, Rev. Reuter; the Bawenda, Rev. Gottschling; report on Zimbabwe, Mr. MacIver; the Basuto, H. E. Mabile.

Section I (Physiology).—**Cape Town**: Discussion on the effect of climate on health, opened by Sir T. Lauder Brunton (Dr. David Ferrier, Prof. McKendrick, Dr. Gregory, Dr. Jasper Anderson, Prof. Bohr, and Dr. J. A. Mitchell will take part); so-called scurvy of South Africa, Dr. Gregory; on plague, Dr. J. A. Mitchell; leprosy in Cape Colony, Dr. A. S. Black; South African drugs, Dr. Moberley; discussion on horse-sickness and allied diseases, opened by Dr. Edington (Dr. Hutcheyn, Mr. Du Plessis, Dr. Wm. Robertson, Colonel Bruce, and Prof. Sims Woodhead will take part); stock diseases in South Africa, Dr. Hutcheon; ticks as a means of conveying disease in South Africa, Mr. Lounsbury. **Johannesburg**: President's address; horse-sickness, Dr. Theiler; rinderpest, Dr. G. Turner; a discussion on lung diseases in connection with mining (Dr. Sims Woodhead) is under consideration; nervous diseases, Prof. Ferrier; the life-history of coloured labourers in the Transvaal, Dr. D. Macaulay and Dr. Louis Irvine; dysentery, Colonel Cecil Birt.

Section K (Botany).—**Cape Town**: The present position of our knowledge of seaweeds, Prof. R. W. Phillips; the fossil floras of South Africa, A. C. Seward; educational methods in the teaching of botany, Harold Wager; notes on irrigation farming on the Orange River, F. B. Parkinson. **Johannesburg**: President's address; photography as an aid to oecological research, Prof. F. E. Weiss; the problems of heredity, R. P. Gregory. It is expected that Prof. Engler, Prof. Pearson, and others will contribute papers.

Section L (Educational Science).—**Cape Town**: President's address; the teaching of science, Prof. H. E. Armstrong; the teaching of science in South Africa, Dr. Hahn; rural education, appropriate to colonial life in South Africa, and agriculture, A. D. Hall; the higher education of women in South Africa, Miss Clarke; disabilities of South African school-boys, W. A. Way; Cape education, its difficulties and development, Rev. W. E. C. Clarke. **Johannesburg**: Changes in the Dutch language since its introduction into South Africa, Dr. Brill; education on the veldt, Mr. Corbett; prospects of secondary schools in the Transvaal, Mr. Hope; teaching of agriculture, F. B. Smith; native education, Hobart Houghton; progress of education in the Transvaal, H. Warre Cornish; education in Rhodesia, G. Duthie; a school of forestry, T. R. Simms; the teaching of architecture, R. G. Kirkby; education in the Orange

River Colony, Hugh Gunn; manual instruction in the Transvaal, T. Lowden; recent improvements in the training of infants, with special reference to South Africa, Miss Weldon; discussion with Section A, the teaching of elementary mathematics.—*Nature*.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 30th, 1905.

Dr. R. T. GLAZEBROOK, F.R.S., Past-President in the Chair.

A PAPER ON "The Comparison of Electric Fields by means of an Oscillating Electric Needle" was read by Mr. D. OWEN.

This paper describes experiments which show how an "electric needle" may be used to measure electric fields in a manner similar to that in which a magnetic field is measured by an oscillating magnetic needle. The needles used were cylindrical in form, of aluminium or of brass, and were suspended by quartz fibres three or four inches in length. The couple on the needle when disturbed from the direction of the field is proportional to the square of the field strength. For small displacements the needle vibrates isochronously, the frequency being proportional to the electric force. It may be used in alternating as well as in steady fields, and may be applied to illustrate many of the laws of electrostatics. The disturbing effect of the needle upon the field is considered; in particular its effect when placed in a uniform field. It is shown by experiments that the disturbing effect falls off rapidly with the distance from the needle, and is inappreciable (in the case of a needle $1\frac{1}{4}$ cms. long) at a distance of twice the length of the needle. With regard to the effect of the dimensions of the needle upon the frequency (for given field), while the restoring couple decreases rapidly with decrease of size, yet the moment of inertia decreases more rapidly, so that the smaller the needle the greater the frequency and also the smaller the disturbing effect. The shielding effect of some dielectric materials was examined in the following way:—A needle was suspended centrally in the uniform field between a pair of parallel plates. A thin walled cylinder of the dielectric was placed around the needle, and the shielding action denoted by a fall in frequency of the needle. Glass and mica were found to effect perfect shielding. Ordinary paper shields; but when thoroughly dried by heat the electric field is transmitted undiminished only to fall off to zero after a minute or two's exposure to the air. Dry paper soaked in melted paraffin-wax transmits the field perfectly and for an indefinite time. The paper concludes by pointing out that an electric needle suspended between a pair of parallel plates forms a simple means of measuring high voltages, since the frequency of vibration is simply proportional to the voltage between the plates.

Prof. R. W. WOOD read a paper on "The Magneto-Optics of Sodium Vapour and the Rotatory Dispersion Formula."

It has been shown in a previous paper that the vapour of metallic sodium is an ideal substance for investigating the effect of a strong absorption band on the magnetic rotation of the plane of polarisation. The preliminary work was not very satisfactory, as the method employed did not admit of very accurate determinations of the wave-lengths. Improvements in the methods of observation and design of the apparatus have been accompanied by an increase in accuracy, and accurate readings have been obtained for as many as nine different values of λ between D_1 and D_2 . Rotations as great as 1440° (four complete revolutions) have actually been observed, and this with a 10 c.m. column of not very dense vapour in a field of 2000 C.G.S. units. In the present paper the magneto-optics of the

vapour for light travelling along the lines of force are discussed. The sodium was heated in a tube of thin steel, the ends of which projected from the helices of the magnet. It was found that the field strength within the steel tube did not differ greatly from that obtained when glass tubes were used. A short piece of small brass tubing is brazed into one end of the steel tube, through which the steel tube is exhausted. A good vacuum is essential, all traces of rotation disappearing in hydrogen or nitrogen at atmospheric pressure. Light from an arc-lamp made parallel by a lens is passed through a Nicol's prism, the steel tube, and a second Nicol, after which it is brought to a focus upon the slit of a spectroscope by means of a second lens. In the present case, a concave grating of 14 feet radius was used instead of a spectroscope, the observations being made both visually and by means of photography. The paper then describes the phenomena which are presented when the sodium vapour is formed in the magnetic field. In the case of very dense vapours the rotation has been measured over a considerable range of wave lengths, namely, throughout the region comprised between $\lambda = 5840$ and $\lambda = 5922$. The rotation constant of D_2 was found to be about double that of D_1 . Drude, in his "Lehrbuch der Optik," has given two formulæ for the magnetic rotatory dispersion, the first of which, developed from the hypothesis of molecular currents, calls for an anomalous effect on crossing the band, and does not apply to sodium vapour. The second, developed from the Hall-effect hypothesis, predicts rotations of similar sign and equal magnitude for wave-lengths symmetrically situated in the spectrum, with respect to the centre of the absorption-band. It seems likely that the molecular currents play some part, and that the formula built up on the hypothesis of the Hall-effect is incomplete. However, the latter formula represents the rotation outside of the D-lines with great accuracy, while between the lines it gives in some cases a curve which is elevated somewhat above the experimental curve. The paper concludes with an account of the bright-line spectrum produced by magnetic rotation which presents itself when the Nicol's prisms of the apparatus are crossed. The spectrum, which at first could only be seen with difficulty, was finally obtained of such brilliancy that it could be photographed with a 14-foot concave grating. A good vacuum was found to be an essential condition, the presence of inert gases causing a faintness of the lines.

Mr. A. CAMPBELL asked if the apparatus could be used to measure magnetic fields.

Prof. R. W. WOOD said there would be difficulty in determining the density of the vapour. It could be used, however, to determine the density of the vapour from a knowledge of the magnetic field.

Prof. R. W. WOOD read a paper on "The Fluorescence of Sodium Vapour."

The fluorescence of sodium vapour has been investigated by allowing light of various wave-lengths to illuminate the vapour, and then studying the light emitted with a spectroscope. Approximately homogeneous light of any desired wave-length is obtained by means of a monochromatic illuminator. Some sodium is placed in a horizontal steel tube fitted with steel ends, in one of which is a circular aperture bored just above the centre. The tube is heated and the vapour rises until it reaches the hole. The light from the monochromatic illuminator passes through the hole and falls upon the vapour. The fluorescent light is then observed by means of a spectroscope either visually or by photography. It is essential that the incident light should not traverse an appreciable amount of the vapour, or the fluorescent effects are masked by those of absorption. The bright lines of the fluorescent spectrum are by no means the exact complement of the absorption spectrum. Very remarkable effects have been observed when the vapour is illuminated with a very narrow band of approximately homogeneous light, the lines in the fluorescent spectrum changing their position and appearing to dance about with the slightest change

in the wave-length of the exciting light. The motion is of course only an illusion, lines disappearing and others re-appearing, like the sparks of a spintharoscope. Stokes's law is violated in a most flagrant manner, bright lines coming out on both sides of the excited region. The behaviour of the spectrum indicates that we are dealing with a number of groups of electrons, each group containing a large number of vibrators. The excitation of one of these vibrators sets the whole group going, but does not start disturbances in the other groups.

ROYAL SOCIETY OF NEW SOUTH WALES.

Annual General Meeting, May 3rd, 1905.

Prof. LIVERSIDGE, M.A., LL.D., F.R.S., Vice-President, in the Chair.

THE following gentlemen were declared duly elected Officers and Members of Council for the current year:—

President—H. A. Lenehan, F.R.A.S.

Vice-Presidents—Prof. Liversidge, LL.D., F.R.S.; Prof. Warren, M.Inst.C.E., Wh.Sc.; F. B. Guthrie, F.I.C., F.C.S.; F. H. Quaife, M.A., M.D.

Hon. Treasurer—D. Carment, F.I.A., F.F.A.

Hon. Secretaries—J. H. Maiden, F.L.S.; G. H. Knibbs, F.R.A.S.

Members of Council—S. H. Barraclough, B.E., M.M.E.; Prof. T. W. E. David, B.A., F.R.S.; H. Deane, M.A., M.Inst., C.E.; T. F. Furber, F.R.A.S.; W. M. Hamlet, F.I.C., F.C.S.; T. H. Houghton, M.Inst.C.E.; H. C. Russell, B.A., C.M.G., F.R.S.; Henry G. Smith, F.C.S.; Walter Spencer, M.D.; J. Stuart Thom.

The following letter was received from Mr. L. W. MARCKER, Consul for Denmark:—

Consulate of Denmark, Sydney, N.S.W.,
February 9th, 1905.

SIR,—The sympathy which has been shown by men of science from all parts of the world over the death of the young Danish scientist Professor Mills R. Finsen, and the numerous foreign enquiries which have been made, asking permission to take part in the movement started in Denmark to raise funds, according to the deceased's last wish, to enable the scientific institution called the Finsens Institute (to which Finsen presented the Nobel prize won by him) to continue the researches so ably begun by him, has resulted in that the original Danish Committee now has become a universal one. Sub-committees have been started in England, all over the Continent, and in America. At the request of the Danish Committee, the Consulate has received instructions from the Ministry for Foreign Affairs, Copenhagen, to place the matter before the scientific bodies in Sydney. I therefore herewith have the honour to request you kindly to be good enough to direct the attention of the members of your honoured Society to the movement. The Consular instructions are also to give any local movement which might be started all possible assistance, and I need hardly say that any information or help I can give will be given with very great pleasure.—I have, &c.,

L. W. MARCKER, Consul.

Messrs. J. H. Maiden and G. H. Knibbs,
Hon. Secretaries, Royal Society of N.S. Wales.

The following papers were read:—

"On the Occurrence of Calcium Oxalate in the Barks of the Eucalypts." By HENRY G. SMITH, F.C.S., Assistant Curator, Technological Museum, Sydney.

The author announces the presence, in large quantities, of calcium oxalate in the barks of several species of Eucalyptus. It is similar in form and appearance in all species, being well defined monoclinic crystals in stout microscopic prisms, averaging 0.0174 m.m. in length and 0.0077 m.m. in breadth, and containing one molecule of

water. A peculiarity of these is the tendency to form twins geniculate in appearance; twinned forms being pronounced in some species. From botanical and chemical evidence it is assumed that *Eucalyptus salmonophloia* of West Australia and *E. oleosa* of New South Wales belong to the same species, and that the latter tree, which most often occurs as a "Mallee," is only the degenerate stage of the former. The theory is advanced that some of the "mallees," or shrubby Eucalypts, have been formed through the poisoning effect of the excess of oxalic acid, acting for a long time upon species which originally grew as large trees. The tannins in those Eucalyptus barks containing a large amount of calcium oxalate are of very good quality, light in colour, astringent, easily soluble, and should make leather of good quality. On evaporating the extract to dryness on the water-bath but little darkening takes place, and the product is still readily soluble. This class of Eucalyptus barks should, therefore, make excellent tanning extracts. From the bark residue the calcium oxalate should be profitably extracted, and the oxalic acid obtained cheaply from this practically as a by-product. The air-dried bark of *Eucalyptus salubris*, the "Gimlet" of West Australia, gives 30.5 per cent of total extract and 18.6 per cent of tannin absorbed by hide powder, and contains 16 per cent of calcium oxalate. The bark of *Eucalyptus gracilis* contains 16.66 per cent of calcium oxalate; that of *E. Behriana* 16.5 per cent; of *E. oleosa* 10.64 per cent; of *E. dumosa* 9.8 per cent; and of *E. salmonophloia* 8.34 per cent. The barks of all the Eucalypts tested contain calcium oxalate, although in some species in very small amount.

"Notes of Astronomical Interest, dealing with the past Eighteen Months, showing the Progress and Deductions made during that Period." By H. A. LENEHAN, F.R.A.S., Acting Government Astronomer.

OBITUARY.

PROFESSOR P. T. CLEVE,

WE regret to announce the death of Prof. P. T. Cleve, of Upsala, Sweden, which took place on June 18th last. Prof. Cleve was only sixty-five years of age, having been born in 1840. He was the leading scientific chemist in Sweden, but his fame is world-wide. His name will be chiefly known and remembered in connection with his researches on the rare earths, though his work in other departments of science, such as biology and hydrography, was of considerable importance. His first scientific paper was published in the year 1861, and since that time he has contributed a large number, on varying subjects, to different scientific societies and journals. He was an Honorary Member of the Royal Institution and Honorary Fellow of the Chemical Society.

CORRESPONDENCE.

DETERMINATION OF SUGAR BY MEANS OF FEHLING'S SOLUTION.

To the Editor of the Chemical News,

SIR,—In the CHEMICAL NEWS (vol. xci., p. 299) you publish an article upon the "Determination of Sugar by Means of Fehling's Solution," by F. P. Lavalle.

Of course the use of KOH or NaOH is well known, and reference is made to it on page 477 of the Ninth Edition of "Analyse des Harns," by Huppert and Thomas. In the *Chem. Centralblatt*, of 1879, p. 406, Hehner states that the titre of Fehling's solution depends very much upon the percentage of alkalis present, and he is perfectly

correct in asserting that an excess of alkalis should be avoided. In the case of minute quantities no accuracy of results can be obtained by the volumetric method, and it is better to employ Soxhlet's method, which gives exact results in the hands of an experienced analyst.

If, however, the volumetric method is preferred, and difficulty is found in precipitating the cuprous oxide, as, for instance, in the case of beet-sugars, a good result is often obtained by the addition of about 2 c.c. of a normal solution of chloride of calcium.

This expedient is not a new one, but perhaps not generally known.—I am, &c.,

F. M. MRAZSEK.

29, Mincing Lane, E.C., July 8, 1905.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 24, June 13, 1905.

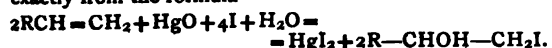
Action of Fluorine on Oxides of Nitrogen.—Henri Moissan and Paul Lebeau.—The authors make a systematic investigation of the action of fluorine on the oxygen compounds of nitrogen. After a certain number of preliminary experiments they discovered that these reactions are very complex, especially that of fluorine on nitrogen peroxide. In other cases this latter body is formed in a great number of transformations of the nitrogen compounds, and its intervention furnishes secondary reactions which complicate matters considerably.

The True Atomic Weight of Nitrogen.—G. D. Hinrichs.—The author's recent experiments, and also those performed in 1901, lead him to believe that the atomic weight of nitrogen as compared with oxygen 16 differs very slightly from 14.

A Method of Preparing Acetol and Pyruvic Acid by the Direct Oxidation of Acetone.—M. Pastureau.—By oxidising acetone by means of concentrated hydrogen peroxide, Wölfenstein obtained the superoxide $(C_3H_6O_2)_3$. Baeyer and Villiger, under slightly different conditions, obtained the superoxide $(C_3H_6O_2)_2$. By using a 2 per cent solution of hydrogen peroxide for the oxidation of the acetone the author obtains, besides the superoxide $(C_3H_6O_2)_2$, acetol and pyruvic acid. He also examines the reaction of hydrogen peroxide in acid solution on other acetones, particularly on diethylketone, methylpropylketone, and methylphenylketone, and in all cases observes the formation of acetone superoxides, ketonic alcohols, and ketonic acids.

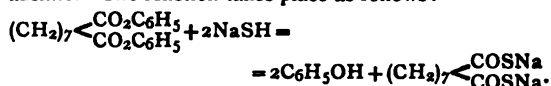
Action of Sodium on the Ethers of Monobasic Acids of the Fatty Series of Simple Function.—M. Bouveault and R. Locquin.—Sodium reacts on the ethers of the monobasic acids of the fatty series in presence of alcohol or water, in a very definite manner, and it seems probable that the reaction of the sodium and of the ether alone should be definite also, and that the bad results obtained in previous experiments are due to defective experimental conditions.

Mono-substituted Aromatic Oxides of Ethylene.—MM. Fournneau and Tiffeneau.—The 1.2-mono-substituted ethylene oxides can easily be obtained from the corresponding ethylenic derivatives. The latter substances in presence of aqueous ether are acted upon by iodine, and the yellow oxide of mercury in proportions calculated exactly from the formula—



Action of Chloroacetic Ethers on the Halogen-magnesium Derivatives of Aniline.—F. Bodroux.—The action of ethyl chloroacetate on magnesium phenylamine iodide is effected in two different parts. One portion of the reagent acts on the ether-salt function, and by its own atom of chlorine produces the complex which ultimately gives iodoacetanilide. The other portion acts only through its halogen atom, and gives the ethyl iodoacetate, which persists in the mixture, and later contaminates the solid product of the operation. The result is quite different when ethyl chloroacetate and magnesium-phenylamine bromide is used. Chloroacetanilide only is formed in this case, $C_6H_5-NH-CO-CH_2Cl$.

Certain Compounds of Azelaic Acid.—A. Bouchonnet.—The author prepares thioazelaic acid from phenyl azelate. The reaction takes place as follows:—



The thioazelate of sodium thus obtained when treated with HCl gives the free acid, $(CH_2)_7 \begin{smallmatrix} COSH \\ COSH \end{smallmatrix}$.

Sparteine; its Action on Methyl Iodide.—Charles Moureu and Amand Valeur.—As a result of the authors' experiments on sparteine, the detail of which will be published later, they find that methyl iodide when acting upon sparteine always produces, besides the iodomethylate, which is already known, an isomer which differs chiefly in its much greater rotatory power and its extreme solubility in water.

Pyrolysis of Gum-lake.—A. Etard and E. Wallée.—The authors experiments give definite and abundant results which tend to throw some light on the constitution of resins, substances which have hitherto been somewhat neglected. There exists both an acetate of bornyl and other analogous terpenic ethers. Apparently the numerous resins seem to be the ethers of the higher acids and of the polyterpenes. Gum-lake should therefore be comparable with artificial drying compounds used as protection agents. Experimentally, this substance seems to be a non-stable oleate of a continuous series of polyterpenes. In an isolated form these drying agents are contained in a large number of vegetable species, and combined they form the base of commercial varnishes.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Baroness Gray was elected a Member. The Special Thanks of the Members were returned to Sir Andrew Noble, K.C.B., F.R.S., for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures; and to Mr. Rollo Appleyard for his gift of a Portrait of the late Professor J. D. Everett, F.R.S., M.R.I.

American Chemical Society, June 22 to 24, 1905, Buffalo, N.Y.—The following is a list of papers read:—

"The Classification of Carbon Compounds." Marston T. Bogert.

"Some Recent Advances in Physiological Chemistry." John H. Long.

"Note on the Atomic Weight of Carbon." C. L. Parsons.

"Chemical Glassware." Percy H. Walker.

"An Apparatus for Determining the Viscosity of Liquids at Different Temperatures." F. Courtois.

"An Apparatus for Determining the Flash-point of Inflammable Liquids." F. Courtois.

- "Vapour Pressure of Sulphur at 100°." (Second paper). Hippolyte Gruener.
- "On a New Dynamic Method of Measuring Vapour Tensions of Solutions." Louis Kahlenberg.
- "Molecular Weight by Vapour Heating." H. R. Carveth and J. P. Magnusson.
- "The Hydrolysis of Ammonium Acetate and the Ionisation of Ammonium Hydroxide and Water at High Temperatures." A. A. Noyes and Yogoro Kato.
- "The Constitution of the Bronzes." W. D. Bancroft.
- "Tensile Strengths of Aluminium Zinc Alloys." W. D. Bancroft.
- "Some Alloys of Zinc." W. D. Bancroft.
- "A New Use for the Dilatometer." W. Lash Miller.
- "Equilibrium in the System $\text{BeO}:\text{CaO}_3:\text{H}_2\text{O}$." C. L. Parsons and W. O. Robinson.
- "The Phosphates of Calcium." F. K. Cameron.
- "The Application of Physical Chemistry to Soil Studies." F. K. Cameron.
- "The Transmutation of the Elements." H. T. Barnes.
- "A Strong Sterilisable Dialysing Membrane." H. W. Hill.
- "Some Notes on Rock Decompositions." A. S. Cushman.
- "Some Observations on the Deposition of Alloys from from Mixed Solutions." C. B. Jacobs.
- "Some Properties of the Metal-ammoniums." C. A. Kraus.
- "A Determination of the Coefficient of Expansion of Oxygen." Edward W. Morley and Dayton C. Miller.
- "The Isolation and Properties of some Electro-positive Radicals." C. A. Kraus.
- "The Precipitation of Colloidal Egg Albumin by Electrolytes." A. P. Matthews.
- "On the Solubility of Carbohydrates in Pyridine and the Optical Rotatory Power of the Resulting Solutions." J. G. Holty.
- "On the Dielectric Constants of certain Solvents and Solutions." J. H. Mathews.
- "Some Absorption Phenomena with Phosphates." Oswald Schreiner.
- "Dimeric Equilibria." W. D. Bancroft.
- "A Manostat." W. D. Bancroft.
- "The Constitution of Trinidad Asphalt from a Physico-chemical Point of View, and its Proximate Composition." Clifford Richardson.
- "The Action of Ethylene Dibromide on *p*-Nitrosodialkylanilines." Henry A. Torrey.
- "On the Preparation of Various Acyl Derivatives of Dimethyl 4-Amino-*o*-phthalate." M. T. Bogert and R. R. Renshaw.
- "On some Nitro- and Amino-derivatives of Fluorescein." (Preliminary Notice). M. T. Bogert and R. G. Wright.
- "Researches on Pyrimidines: On 2, 5-Diamino-6-oxypyrimidine." Treat B. Johnson.
- "On the Constitution of Phenylurazole." S. F. Acree.
- "On the Pinacone-pinacolin Re-arrangement." S. F. Acree.
- "The True Benzaldehyde-azo-benzoic Acids." Frederick J. Alway.
- "The Neutral Sulphite Method for Determining Aldehydes in Essential Oils." S. S. Sadtler.
- "The Detection and Determination of Ethyl and Methyl Alcohols in Mixtures by the Immersion Refractometer." Albert E. Leach.
- "A Comparison of Methods for the Determination of Fusel Oil." E. M. Chace and W. L. Dubois.
- "A Crucible Method for the Determination of Sulphur, Halogens, and Phosphorus in Organic Substances." S. S. Sadtler.
- "Methods for Examinations of Cellulose-nitrate and Smokeless Powders." Albert P. Sy.
- "Camphoroxalic Derivatives." J. Bishop Tingle and W. E. Hoffman, jun.
- "Rosocyanine." C. L. Jackson and Latham Clarke.
- "The Formula of Curcumine." C. L. Jackson and Latham Clarke.
- "The Reduction of 5-Nitro-4-ketodihydroquinazolines to the Corresponding Aminoquinazolines, and the Preparation of certain Derivatives of the latter." M. T. Bogert and V. J. Chambers.
- "The Synthesis of 5-Nitro-4ketodihydroquinazolines from 6-Nitroacetantranil and Primary Amines." M. T. Bogert and H. A. Seil.
- "On Isomeric O and N Ethers Derived from 2-Alkyl-4-oxy-5-nitroquinazolines and 2-Alkyl-4-keto-5-nitrodihydroquinazolines." M. T. Bogert and H. A. Seil.
- "Some Acyl Derivatives of Homoanthranilic Nitrile and the 7-methyl-4-ketodihydroquinazolines Prepared therefrom." M. T. Bogert and A. Hoffman.
- "The Condensation of Succinylosuccinic Acid Diethyl Ester with Guanidine: A Derivative of 1, 3, 6, 8-Naphthotetrazine, a New Heterocycle." M. T. Bogert and A. W. Dox.
- "The Methoxyl Group in certain Lignocelluloses." Alvin S. Wheeler.
- "Milk Proteids and some of their Relations." L. L. Van Slyke.
- "The Physiology of Uric Acid." F. H. McCrudden.
- "Adrenaline, the Active Principle of the Suprarenal Glands." T. B. Aldrich.
- "Convenient Distillation Arrangements for Free and Albuminoid Ammonia." W. F. Mason.
- "The Purification of Water by Ozone." R. S. Weston.
- "The Purification of Water by Copper." W. H. Buhlig.
- "Colloidal Suspensions and their Relation to Problems in Water Purification." J. W. Ellms and J. F. Snell.
- "The Composition of Cooked Foods." W. D. Bigelow.
- "Artificial Digestion Experiments." Edward Gudeman.
- "Notes on Occurrence of Pentoses in Second Pressing Cider." J. A. Le Clerc and L. M. Tolman.
- "Color Tests for Cod-liver Oil." W. D. Bigelow.
- "The Presence of Hexone Bases in Bacteria." Mary F. Leach.
- "The Chemistry of Flesh." H. S. Grindley.
- "Unfermentable Matter in Glucose and Grape Sugar." A. P. Bryant.
- "The Testing of Wheat Flour for Commercial Purposes." Harry Snyder.
- "The Occurrence of Extractives in Apple-peel." H. C. Gore.
- "The Pecto-celluloses of the Apple." W. D. Bigelow and H. C. Gore.
- "A Study of the Unfermentable Reducing Matters in Hydrolytic Product of Starch." A. P. Bryant and C. S. Miner.
- "Laboratory Methods for Studying the Formation of 'Alkali.'" F. K. Cameron.
- "The Analysis of Sugar Mixtures." C. A. Browne, jun.
- "Chemical Preservatives Used in Food Products. Are they Harmful?" E. W. Duckwall.
- An Address by Victor Lenher. Subject, "Tellurium."
- "Recent Work on Columbium and Tantalum." R. D. Hall.
- "On the Oxidation of Hydrazine." Arthur Wesley Browne.
- "Qualitative Analysis, its Place and Importance in Chemical Instruction." Edward Ellery.
- "The Chemical Separation of the Radio-active Types of Matter in Thorium Compounds." Herman Schlundt and Richard B. Moore.
- "On the Radio-activity of the Mineral Waters of Missouri." Hermann Schlundt and Richard B. Moore.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Ozone—I am in search of a book on Ozone, and should be extremely obliged if any correspondent could tell me of such a book. I have one by Emile Andreoli (published by H. Alabaster, 1893), which is, however, of no use to me. We are thinking of having an ozone bleaching plant, and wish to know something about ozone generally before adopting it.—OZONE.

Reclaiming Waste Rubber.—(Reply to "Waste Rubber").—Possibly the enquirer may find what he wants in my translation from the French of "Indiarubber and Gutta-percha," by T. Seeligmann, G. L. Torrilhon, and H. Falconnet (Scott, Greenwood, and Co.), i.e., if he can get a copy, as it is, I believe, almost if not quite out of print. With that book and the abridgments of patents (to be had *ad initio* for a nominal sum) I do not think any insurmountable difficulty will be encountered. Working with acids, lead-lined (i.e., lead burned) vessels will of course be necessary—and possibly these can be got as cheap and as well burnt as anywhere from Mr. Pitt, Chemical Plumber or Lead Burner, Ferry Street, Millwall, London, E. I would advise the enquirer to consult Mr. Pitt by appointment, if resident in London; or if he shows the diagrams of plant in Patent Office specifications (expired patents, of course) to any local lead burner, he will readily construct an apparatus for him. He must take care he does not get into trouble with the local authorities in regard to fumes. I do not now exactly remember whether such works come under any Local Government Board regulations or not; in any case they should. But rubber reclamation is too wide a subject to answer in a Note, but if the enquirer wants any specific information I am at his disposal through your columns.—JOHN GEDDES MCINTOSH, 9, Parsonage Street, Cubitt Town, E.



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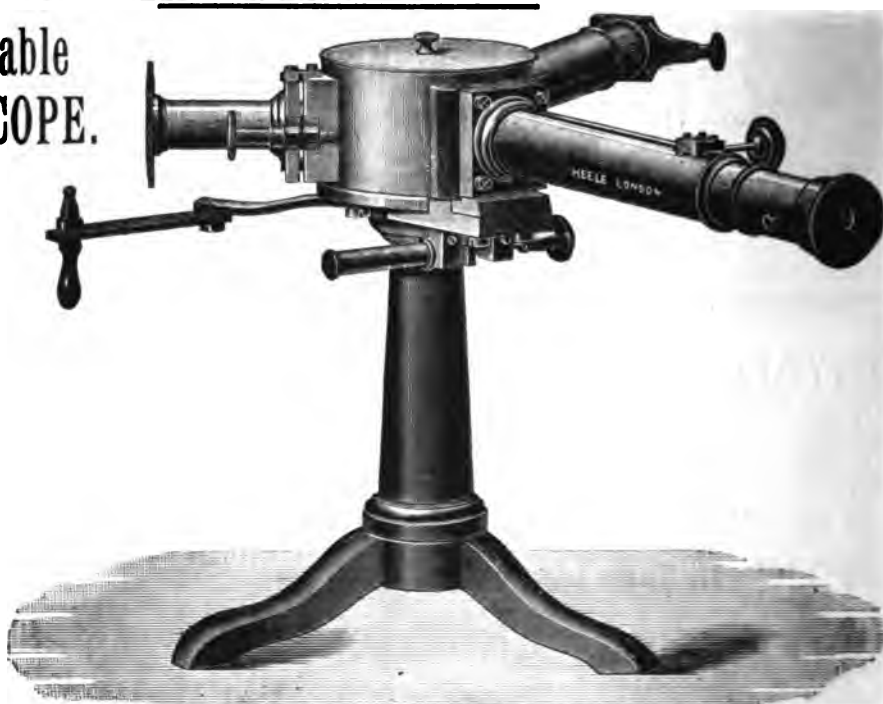
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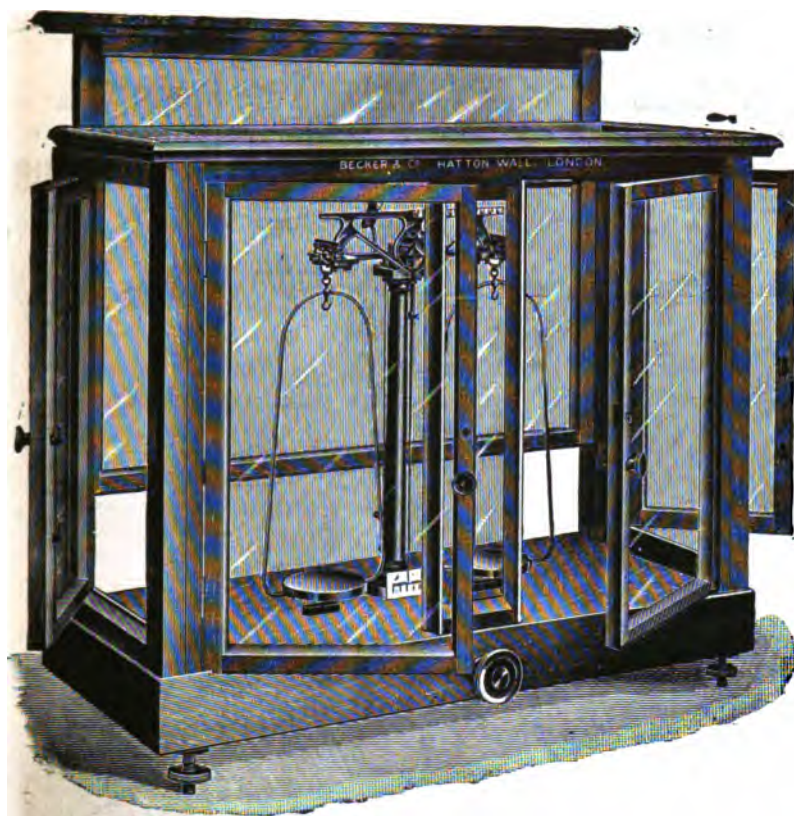
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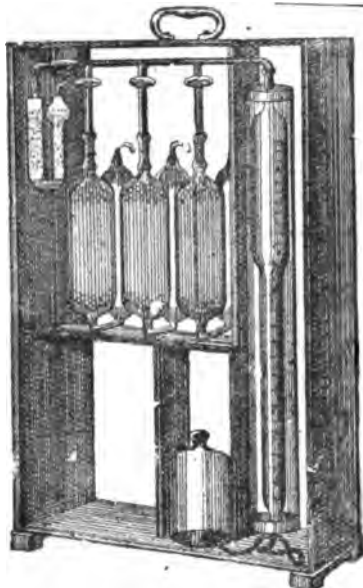
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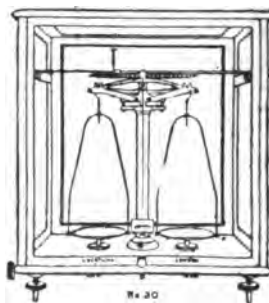
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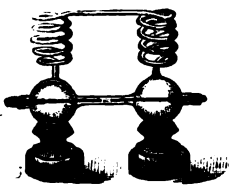
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THE CHEMICAL NEWS.

VOL. XCII., No. 2382.

ON THE PHOSPHORESCENT SPECTRA OF Sd AND EUROPIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

THE recent examination of a pure specimen of europium prepared by M. Urbain has brought to light some interesting facts connected with its phosphorescent spectrum when the sulphate is subjected to cathode radiations in a radiant matter tube.

In Demarçay's paper announcing the discovery of europium (*Comptes Rendus*, cxxxii., p. 1484; *CHEMICAL NEWS*, lxxxiv., p. 1), he referred to the phosphorescent spectrum of the new earth in the following terms:—

"In 1885 Sir William Crookes, during his beautiful researches on electric phosphorescence *in vacuo*, noticed a band which he attributed to samarium, and which, by reason of its disappearance in the presence of lime and from certain other peculiarities, he called the 'anomalous line.' Later he distinguished this, together with a large number of other bands, as belonging each to a special meta-element. The hypothetical meta-element corresponding to the anomalous line he called Sd. M. Lecoq de Boisbaudran, in the course of his important researches on phosphorescence, confirmed the above statements with regard to this anomalous line. In 1892 M. de Boisbaudran described a spectrum consisting of three brilliant blue lines discovered in the spark spectrum of samarium. He concluded that they corresponded to a particular element, Z₁. About the same time he also drew attention to a particular band in the reversal spectrum of samarium, which apparently corresponded to the anomalous line. M. de Boisbaudran, without forming very precise conclusions, inclined to the idea that this line was due to a particular element, Z₂. In 1896 I discovered the presence of an element intermediate between gadolinium and samarium. In 1900 I showed that this new element was identical with de Boisbaudran's Z₁, and that Crookes's anomalous band was due to the same substance, as well as the reversal line Z₂. . . . Since that period, by a long series of fractionations with magnesium nitrate, I have been able to accumulate a considerable quantity of this element. The apparently contradictory results of Crookes and de Boisbaudran are due, I think, to the very small proportions of Z—Z₁ contained in their material. I propose the name Europium for the new element, with symbol Eu, and atomic weight 151 (approx.)."

Immediately on the publication of Demarçay's paper I gave reasons why my earth giving the very sharp red phosphorescent line (which I had called "the anomalous line"), was not the same as either de Boisbaudran's or Demarçay's earth. I said (*CHEMICAL NEWS*, vol. lxxxiv., p. 2, July 5, 1901):—

"It is necessary for me to make one or two corrections to the paper of M. Demarçay.

"I have never admitted that the body called by M. de Boisbaudran Z₁ is the same body which gives my 'anomalous line.' Indeed, I have good reason to think they are quite different. The line given by M. de Boisbaudran's Z₁ is broad and indistinct at the edges, while the 'anomalous line' is absolutely sharp and narrow, like a gas-line. Also their refrangibilities are not identical. The same remarks will apply to the body described by M. Demarçay in his 1900 paper."

The first record of the observation of the so-called anomalous line is in my paper "On Radiant Matter Spectroscopy—Part II., Samarium," read before the Royal Society, June 18, 1885 (*Phil. Trans.*, Part II., 1885), which contains an account of the conditions under which this line is obtained and my reasons for supposing it to be indicative of an elementary substance. In Paragraph 146, I said:—

"It was interesting to ascertain what spectrum a mixture of samarium and yttrium would give. . . . I next tried a mixture of samaria 80, and yttria 20. The spectrum was identical with the one last observed, with one striking difference—the $\lambda = 2693$ line now shines out with great brilliancy of a fine orange-red colour, as sharp as a gas line, and so unlike the bands usually met with in the spectra of phosphorescent earths as to suggest the explanation that some other spectrum-forming body was present in the mixture."

Again, in the same paper, Paragraph 165, I wrote:—

"The Anomalous Line $\lambda = 2693$.—On several occasions I have spoken of an orange line, $\lambda = 2693$, which by its brilliancy and sharpness is a prominent object in most of the samarium-yttrium spectra. With samaric sulphate it is exceedingly faint. With samaria containing 5 per cent of yttria it is very little brighter; . . . and with a mixture of 80 parts samaria and 20 parts yttria it is at its maximum intensity."

The next year I returned to the subject, and in a paper "On some New Elements in Gadolinite and Samarskite, Detected Spectroscopically (*Proc. Roy. Soc.*, June 9, 1886, vol. xl., p. 502), I said that I had since further investigated the occurrence of line $\lambda 6094$, "the anomalous line," with the bringing to light of some important new facts. I found that the body giving rise to the line closely followed samarium in my fractionations, and that the presence of yttria was not necessary to bring it out, the yttria acting only by deadening the brightness of the other red, green, and orange bands of samaria, while it had little or no action on the anomalous line. Again, I found that the addition of a little lime entirely suppressed line $\lambda 6094$, while it brought out the samarium lines with increased vigour. I further found that in samaria prepared from different minerals the line varied greatly in intensity. The earth from samarskite showing it strongly, while samaria from gadolinite showed no trace of line $\lambda 6094$. "It follows, therefore, that the body whose phosphorescent spectrum gives line $\lambda 6094$ occurs in samarskite but not in gadolinite; thus it cannot be due to samarium, yttrium, or a mixture of these two elements. The only other probable alternative is that the source of this line is a new element."

I said:—"A hitherto unrecognised band in the spectra by absorption or phosphorescence is not of itself definite proof of a new element, but if it is supported by chemical facts, such as I have brought forward, there is sufficient *prima facie* evidence that a new element is present. Until, however, the new earths are separated in sufficient purity to enable their atomic weights to be approximately determined, and their chemical and physical properties observed, I think it is more prudent to regard them as elements on probation." I therefore named the new body Sd, the S recalling the source, samarskite.

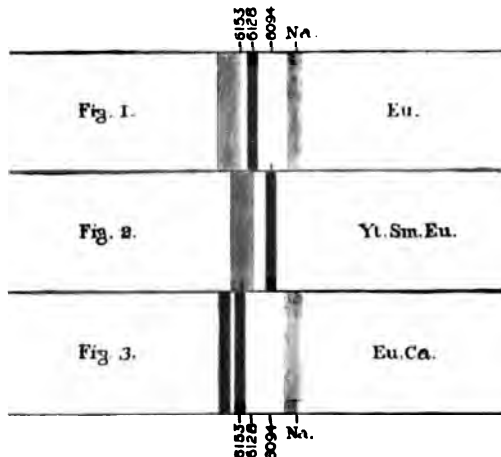
In 1887, I again recurred to the subject of line $\lambda 6094$, and in a paper communicated to the Royal Society on February 10, 1887 (*Proc. Roy. Soc.*, vol. xlii., p. 112), I gave the result of an extended search for the earth which gave rise to it, or Sd. I said that Sd "is not present in the rare earths from gadolinite, xenotime, monazite, hiemite, euxenite, and arrhenite; it is present in small quantity in cerite, and somewhat more plentifully in samarskite. . . . In samarskite yttrium it concentrates at a definite part of the fractionation. A little calcium entirely suppresses the orange line, while samarium or yttrium seem to intensify it."

Owing to want of material and pressure of other occupations, the subject was put aside until recently, when an examination of the phosphorescent spectrum of Urbain's

* A Paper read before the Royal Society, June 8, 1905.

pure europium, in the form of ignited sulphate, led me to take up the matter once more.

Europium sulphate phosphoresces red, as described by Demarçay. A photograph showed a complete absence of phosphorescence bands between λ 4800 and λ 2536. The visible spectrum consists almost exclusively of two red lines, the most refrangible being nebulous and faint, the other sharper and very bright (Fig. 1), and a faint nebosity in the position of the sodium line.



The strong phosphorescent line, which Demarçay thinks is identical with my S δ , is shown by europia and gadolinia; indeed, it is stronger in gadolinia than in europia. Careful measurement shows it is not coincident with the old anomalous line, the wave-length of the europia line being λ 6128 and that of S δ λ 6094.

Experiments were made in connection with the appearance of S δ and the identity or non-identity of it with the similar looking line in Urbain's earths. Some good yttria was mixed with pure samaria in the proportion originally found to give the S δ line most brilliantly, but the phosphorescing sulphate failed to show any trace of it. To this mixture was now added a little europia, and the S δ line was developed brilliantly, and occupied its normal position at λ 6094 (Fig. 2), in a different position to the line seen when the europia is not contaminated with Yt and Sm. This result was so unusual that both tubes, one containing europium sulphate, and the other Eu, Yt, and Sm sulphate, were arranged so that their two spectra overlapped, when the difference in position was very marked.

It having been found that the addition of lime caused the anomalous line to disappear, it was decided to add lime to pure europia to ascertain its effect. It did not suppress the Eu line, but caused it to shift towards the red to λ 6153, still further away from the position it occupied in mixtures of Yt, Sm, and Eu; and its less refrangible companion, shown faint in Figs. 1 and 2, increased to almost equal intensity (Fig. 3).

Sparteïn. Stereoisomerism of the Two Iodomethylates.—Charles Moreau and Amand Valeur.—The two isomeric iodohydrates of sparteïn iodomethylate can be decomposed quantitatively, under the influence of heat, into methyl iodide and sparteïn iodohydrate, the action being the same in the two cases. The action of methyl iodide on sparteïn iodohydrate gives rise to two iodomethylates (united with hydriodic acid). In the two isomeric iodomethylates the methyl iodide is fixed on to the same nitrogen atom. It follows from these facts that the isomerism of the two bodies can only be due to a different disposition in space of the radicals round the same atom of nitrogen. In other words, it is of a stereochemical order.—*Comptes Rendus*, cxi., No. 25.

THORIANITE, A NEW MINERAL FROM CEYLON.*

By WYNDHAM R. DUNSTAN, M.A., LL.D., F.R.S.,
and
G. S. BLAKE, A.R.S.M.,
Assistant in the Scientific and Technical Department of the
Imperial Institute.

(Concluded from p. 15).

Composition of Thorianite.

THE methods used in determining the composition of thorianite are founded on those suggested by Glaser (*Zeit. Anal. Chem.*, 1897, vol. xxxvi., p. 213), Meyer and Markwald (*Ber.*, 1900, vol. xxxiii., p. 3003), Fresenius and Hintz (*Zeit. Anal. Chem.*, vol. xxxv., p. 343), and Benz (*Zeit. Ang. Chem.*, 1902, p. 297).

The results are shown in the accompanying table, which includes the data obtained from three separate specimens, numbered I., II., and III.

Analyses of Thorianite.

	I. Per cent.	II. Per cent.	III. Per cent.
Soluble in nitric acid—			
Thorium dioxide	72.24	76.22	78.86
Uranium dioxide	11.19	12.33	6.03
Uranium trioxide	—	—	9.07
Cerium dioxide	6.39	8.04	1.02
Lanthanum and didymium oxides	0.51		
Yttrium oxide	—	—	—
Lead oxide	2.25	2.87	2.59
Ferric oxide	1.92	0.35	0.46
Calcium oxide	—	—	1.13
Helium	—	—	0.39*
Titanium dioxide	—	—	—
Phosphoric oxide	—	—	Trace

Insoluble in nitric acid—

Zirconium oxide	3.68	—	0.20
Silica	1.34	0.12	
Residue from fusion with potassium-hydrogen sul- phate	0.41	—	—

* If the whole of the gas is calculated as helium.

In the estimation of the metals, 2 grms. of the finely powdered mineral were dissolved in about 15 c.c. of nitric acid of specific gravity 1.4, and after decomposition was complete the solution was diluted and filtered. The insoluble residues in specimens II. and III. were very small, and were treated with hydrofluoric acid to estimate silica. In I. the residue chiefly consisted of zircon which was fused with potassium hydrogen sulphate to extract zirconia, and the residue treated as before with hydrofluoric acid to estimate silica. Except for this associated zircon, no zirconia was found in the mineral.

The acid filtrate from the insoluble residue was diluted to about 300 c.c. and 5 c.c. of hydrochloric acid added. Hydrogen sulphide was then passed through the liquid to precipitate lead which was finally weighed as sulphate. The filtrate was boiled to remove hydrogen sulphide, and oxidation of the last traces of this substance effected with bromine water. To the hot acid solution, amounting to about 350 c.c., excess of ammonium oxalate was added, and the precipitate of oxalates of thorium and cerium, &c., allowed to settle overnight and then filtered. The filtrate was evaporated to dryness and treated with nitric acid to destroy oxalic acid, and diluted with water. The calcium and magnesium were separated from other metals by precipitating the latter with ammonia and ammonium chloride. This precipitate was dissolved in hydrochloric acid, excess of acid neutralised, and the solution diluted to 500 c.c. A few drops of solution of sodium sulphite were added, and the liquid boiled to precipitate any titanic acid. No

* A Paper read before the Royal Society, May 18, 1905.

titanium was, however, present. The liquid was evaporated, and the iron oxidised with a few drops of nitric acid. The liquid was neutralised with a few drops of ammonia, and finally excess of ammonium carbonate added. The carbonates first precipitated were re-dissolved on further addition of the reagents, showing the absence of alumina. The iron was separated as sulphide. The filtrate was boiled, acidified with hydrochloric acid, and again boiled to remove all the carbon dioxide. The uranium in solution was preprecipitated with ammonia, and finally weighed as uranosouranic oxide, U_3O_8 .

The precipitate containing the oxalates of thorium and cerium, &c., was dried, and the oxalates were then decomposed by nitric acid, and the metals obtained in solution as nitrates. After diluting to 250 c.c., sodium thiosulphate was added to the slightly acid boiling liquid till no further precipitate of thorium salt was obtained. The liquid was boiled for a short time, the precipitate filtered off and dissolved in hydrochloric acid, and the operation twice repeated to completely separate the cerium. To the united filtrates ammonia was added, and the precipitate of hydroxides of the cerium, &c., containing a little thorium and any yttrium present, was dissolved in hydrochloric acid, and the trace of thorium precipitated as above described from a small bulk of liquid. The thorium precipitates were dissolved in hydrochloric acid, and the thorium re-precipitated as hydroxide and finally weighed as the dioxide ThO_2 . The filtrate from precipitation of the cerium earths with ammonia contains lime if such were present in the original mineral. This was separated as oxalate and weighed as oxide.

Determinations of the equivalent of thorium made with the precipitated dioxide obtained in the course of the analysis of the third specimen (see p. 26) by conversion into the sulphate gave 57.25, corresponding with an atomic weight of 229. The accepted atomic weight of thorium, relative to hydrogen taken as 1, is 230.8.

The solution from which thorium had been thus removed, containing cerium and the associated earths, including any yttrium, was treated with ammonia; the precipitate dissolved in dilute sulphuric acid, and the solution, after neutralisation, saturated with potassium sulphate. No yttrium was found in the filtrate by dilution and addition of ammonia.

The double sulphates of potassium with cerium, and of the associated metals lanthanum and didymium, were warmed with ammonia solution, by which means the earths were obtained as hydroxides. These were dissolved in hydrochloric acid and re-precipitated by potash solution. The hydroxides were washed by decantation, a little potash solution added, and chlorine gas passed until the liquid was saturated. The lemon-coloured hydrated ceric oxide was filtered off, re-dissolved, and re-precipitated as hydroxide, and the cerium weighed as the dioxide CeO_2 . The filtrate containing lanthanum and so-called didymium was acidified with hydrochloric acid, boiled to remove chlorine, and the earths precipitated with ammonia and weighed as the oxides.

The uranous oxide (UO_2) was separately estimated by Hillebrand's method as follows:—One or 2 grms. of finely powdered mineral were introduced into a stout tube together with 20 to 30 c.c. of dilute sulphuric acid, consisting of one part of acid to five parts of water. The air was then displaced by carbon dioxide, the tube sealed off, and then heated to $180^\circ C$. for several hours till decomposition was complete. The solution obtained was diluted with recently boiled water, and the uranous sulphate titrated with potassium permanganate.

The method adopted for the determination of helium and associated gases consisted in decomposing the mineral by means of dilute sulphuric acid consisting of one part of acid to five parts of water (Hillebrand, *loc. cit.*). Ten grms. of the powdered mineral were used, and the gas collected in a gas burette over mercury with the usual precautions. The mixture was heated at 100° . Decomposition at this temperature was almost complete in one day, but the

experiment was allowed to continue for two days to ensure the liberation of all the gas.

The gas collected amounted to 105 c.c. at standard temperature and pressure, which corresponds to 10.5 c.c. of gas, chiefly helium, from 1 grm. of thorianite.

Of the three specimens of thorianite analysed the first was too small to admit of any treatment to separate associated minerals, and proved to contain associated zircon. Specimens II. and III. were separated as far as possible from extraneous minerals, and represent a nearer approach to the single mineral. The highest amount of thorium yet found is nearly 79 per cent, which shows that thorianite is the richest mineral in thorium at present known.

Constitution of Thorianite.

From the analytical results, it will be seen that the constituents other than thorium show, as was to be expected in a mineral of this character, some variation. In Nos. I. and II. cerium dioxide occurs up to the extent of 8 per cent, while in No. III. it becomes almost insignificant. The uranium appears to occur in the condition of both uranous and uranic oxides. It is, however, intended to further investigate this question, since the presence of uranic ochre on the surface of some specimens would indicate that the mineral may have suffered considerable superficial oxidation, and that crystals may be found containing a much smaller proportion of uranic oxide. Of the other oxides present, zirconia in the insoluble residue may be safely classed as an impurity arising from zircons which are invariably found with thorianite, sometimes included within the crystalline thorianite. Silica and ferric oxide may be neglected as contaminations. Leaving out of consideration for the present the oxides of lead and calcium (not a constant constituent) the mineral consists of a large amount of oxide of thorium and a small amount of oxides of uranium, with a smaller and variable amount of cerium oxide, the precise significance of which is at present doubtful.

In the original condition the uranium may have existed entirely as dioxide. There can be little doubt that the dioxides of thorium and uranium, as well as certain of the salts of these metals, are isomorphous. In nature these oxides have not been found in a pure crystalline state, but crystals of each have been obtained artificially. Crystalline thorium was obtained by Troost and Aouvard (*Comptes Rendus*, 1886, vol. cii., p. 1422), whilst studying the relation between the double phosphate of potassium and thorium and that of potassium and zirconium. The phosphates were first obtained by adding to fused potassium orthophosphate, thorium phosphate, or anhydrous thorium chloride. On raising the double phosphate to such a temperature that both alkali and phosphoric acid were volatilised, thorium was obtained in crystals belonging to the cubic system; the cuboctahedron and rhombic dodecahedron being the forms observed (*loc. cit.*). Again, uranium oxide was first obtained in an octahedral form by Wöhler by heating a mixture of uranium oxychloride with sodium chloride and ammonium chloride (*Liebig's Annalen*, 1842, vol. xli., p. 345). Later, Hillebrand repeated the experiment, and obtained practically pure uranium dioxide in black octahedral crystals of a specific gravity of about 11 (*Zeit. f. Anorg. Chemie*, 1893, vol. iii., p. 243).

The hydrate of thorium sulphate $Th(SO_4)_2 \cdot 9H_2O$ is also, according to Rammelsberg (*Berl. Acad. Ber.*, 1886, p. 603), monoclinic in crystalline form and isomorphous with the corresponding hydrate of the uranium salt $U(SO_4)_2 \cdot 9H_2O$.

Our analyses of different specimens of thorianite are hardly sufficiently numerous to enable us to conclude that the oxides of thorium and uranium bear a definite relation to one another in the mineral. It seems probable that the mineral belongs to the class of substances known as isomorphous mixtures, of which the simple form would be represented by the formula XO_2 , where X represents a tetravalent element the dioxide of which crystallises in the isometric system the extremes of which would be UO_2 and ThO_2 .

Thorianite is evidently closely related to uraninite (pitchblende) in constitution. The crystalline form of the two minerals is the same and the constituents of both are similar. Hillebrand's analysis of the Branchville varieties of uraninite, which were stated to be nearly unoxidised, furnished 72.25 per cent of uranium dioxide and only 13.27 of uranium trioxide (*Amer. Jour. Sci.*, 1890, vol. xl., p. 384). Uranium dioxide very readily oxidises on exposure to air, and it was only by completely excluding the air that Hillebrand succeeded in obtaining the pure oxide artificially. It is therefore certain that the natural varieties of the oxide so far examined must have suffered alteration and oxidation, and that originally their principal constituent was uranium dioxide. Most of the massive varieties of uraninite are very impure, and this may account in a large measure for the presence of many oxides in this mineral which appear to have very little in common with the principal constituents. Lead oxide is apparently generally present in thorianite. It occurs in small amount and may be combined as uranate. In the case of thorianite the crystallographic examination has shown that the mineral has crystallised with difficulty, and that it is more or less contaminated with those minerals which crystallised at the same time, as well as with impurities contained in the magma from which crystallisation occurred.

As far as the present investigation has gone it appears probable that thorianite is isomorphous with uraninite, and that in the thorianite of Ceylon some of the thoria is replaced by the corresponding uranium oxide. The evidence, however, is not sufficient to show whether this is a case of isomorphous mixture, as seems probable, or of true chemical replacement.

It is obvious that the mineral is one of exceptional interest, and that it presents many problems for investigation, among them being the question of the possible occurrence of small quantities of hitherto little known or unknown elements.* The material furnishes a satisfactory source of pure thoria, a fact which is of commercial importance as well as of scientific interest.

We have shown that thorianite is chiefly composed of thoria, as at present understood. Baskerville believes that he has obtained evidence that the substance at present known as thorium is composed of more than one element, and that he has separated thoria into three oxides differing in density, and one of which is little, if at all, radio-active. These conclusions have, however, been called in question by Meyer and Gompertz (*Ber.*, 1905, vol. iii., p. 187), who assert that thoria shows no evidence of being other than a single substance.

Determination of the rate of decay of the radio activity of thorianite made in Lord Blythwood's laboratory by Mr. H. S. Allen have shown that this property of the mineral is probably consistent with the thorium, uranium, and small amount of radium present.

The radio-activity of the mineral was measured in a parallel plate apparatus, using sufficient material to entirely cover the lower plate. The observed rate of leak under these conditions was 6900 divisions per minute, equivalent to a current through the apparatus of approximately 5.5×10^{-11} amperes. Thorianite is, therefore, somewhat less active than some of the specimens of pitchblende examined by Madame Curie, whose results with this mineral are as follows:—

Pitchblende from Johanngeorgenstadt	8.3×10^{-11} amperes
" " Joachimstahl ..	7.0×10^{-11} "
" " Pzibran ..	6.5×10^{-11} "
" " Cornwall ..	1.6×10^{-11} "

A series of measurements of the rate of decay of activity of the emanation from thorianite have been made;

* Since this was written Hahn, in a communication to the Royal Society (*Roy. Soc. Proc.*, 1905) has announced the existence in thorianite of a small quantity of a new element, which produces the "thorium emanation." This was separated from the 6 cwt. of the mineral referred to earlier in this paper. It must not be overlooked that the consignment, though apparently worked up as a whole, was doubtless a mixture containing several other minerals than thorianite.

16.5 gms. of the mineral were heated in a hard glass tube, and the emanation, previously dried over phosphorus pentoxide, collected in the testing vessel. It was set aside for 6 hours in order to allow the thorium emanation to decay, and then measurements of the activity were made daily.

The results showed that during the first four days the rate of decay was greater than that observed by Rutherford for radium emanation, but that after this period the rate of decay of activity became identical with that of radium emanation. It is probable that the greater rate of decay during the first four days was due to the presence of thorium "excited activity" which, according to Rutherford, decays to half value in the course of 11 hours, whereas the radium emanation falls to half value only in about 3.7 days.

These results clearly indicate the presence of radium emanation in the "total emanation" from thorianite, and that consequently this mineral must contain radium.

Commercial Value of Thorianite.

Owing to the increasing employment of thoria for the manufacture of incandescent gas mantles, the demand for minerals containing thorium has largely increased. The demand is chiefly met from the deposits of sand containing a small percentage of monazite (phosphate of the cerium metals and thorium) which occur in Brazil and in North Carolina. Owing to the foreign control of these sands, British manufacturers have experienced difficulty in manufacturing thorium compounds. Thorianite is, we believe, the first deposit of a thorium mineral to be discovered on British territory. Consignments of thorianite from Ceylon, containing about 70 per cent of thoria, have been recently sold in this country at the rate of £1500 per ton.

For the manufacture of thorium compounds thorianite possesses the advantage, not shared by any known thorium mineral, of containing uncombined thoria, soluble in nitric acid with formation of thorium nitrate.

THE DECAY CONSTANT OF RADIUM EMANATION.

By O. SACKUR.

THE decay constant of radium emanation has been found by P. Curie (*Comptes Rendus*, 1903, cxxxv., 857) to be 2.02×10^{-6} , and by Rutherford and Soddy (*Phil. Mag.*, 1903, [6], v., 441) to be 2.16×10^{-6} . Hence the time in which the activity of the emanation sinks to half its value is calculated to 3.98 days and 3.71 days respectively. As the determination of the rate of decomposition of the emanation is the most convenient and accurate way of identifying and analytically proving the presence of radio-active elements, it seemed desirable to establish the value of the decay constant of radium emanation as exactly as possible, and to explain the above mentioned difference. This difference might possibly be caused by the difference in the methods employed by the investigators. Thus Curie determined the loss of activity of a closed tube filled with the emanation, its conductivity being thus caused by the emanation itself and by the induced activity formed upon the walls, while Rutherford and Soddy, on the other hand, in each experiment filled the measuring tube with the emanation which was stored in a gasometer, and determined the conductivity directly after it had been blown in, thus before an appreciable amount of induced activity had been formed. Both methods lead to the same values of the decay constant if in each moment the induced activity is proportional to the strength of the emanation, which is generally assumed to be the case. If i denotes the measured activity, L' the part due to the emanation, and i'' that due to the induced activity, then—

$$\begin{aligned} \text{According to Rutherford and Soddy} \quad & i = i' \\ \text{According to Curie} \quad & i = i' + i'' \end{aligned}$$

By the exponential law $i' = i_0 e^{-\lambda t}$, and, moreover, $i'' = ki' = ki_0 e^{-\lambda t}$; thus $i = i_0(1 + k)e^{-\lambda t} = i_0' e^{-\lambda t}$.

As Curie found the exponential law was confirmed in his experiments the assumption of the proportionality of emanation and induced activity is proved, and the value obtained by him is the decay constant of radium emanation.

To determine λ more accurately I employed the experimental arrangement described by Rutherford and Soddy. Some bubbles of radium emanation, which had formed in a solution of 1 m.grm. of radium bromide in 1 c.c. of water, were mixed with about 10 litres of air, thus diluted ten million times, and kept in a gasometer over water. After definite intervals of time (one or more days), a measured volume was drawn off by a gas pipette, dried by a phosphorus pentoxide tube, and introduced into the measuring tube, the conductivity of which was measured first at intervals of a few minutes and then at intervals of quarters of an hour. The current was supplied by an accumulator battery of 200 cells, and a Thomson's electrometer served as the measuring instrument. In the first fifteen minutes the conductivity increases very rapidly in consequence of the induced activity resulting on the walls, and then more slowly till it reaches a constant value after about two hours; the emanation was then expelled.

Table I. shows this increase of conductivity after the measuring tube has been filled. As the gasometer containing the emanation was not in the same room as the electrometer, the first measurement could not be taken sooner than two minutes after filling. The numbers denote the scale divisions which the image of the electrometer needle travels over in ten seconds.

Time after filling.	Conductivity.
Mins.	
2	266
5	282
8	305
11	313
15	317
41	352
71	385
101	403
146	410
160	403

If the corresponding curves are drawn, we can read off with sufficient accuracy what value the conductivity would have after, for example, fifteen, thirty, and sixty minutes. The comparison of these numbers on different days after filling the gasometer gives the decay constant of radium emanation.

Table II. gives these values and the corresponding common logarithms.

Age of the emanation.	Conductivity.			Logarithms.		
	I.	II.	III.	I.	II.	III.
	15 mins.	30 mins.	60 mins.			
Hours.						
0	362	379	404	2.558	2.578	2.606
51	253	266	286	2.402	2.422	2.455
73	200	212	233	2.301	2.325	2.367
146	123	129.5	136	2.085	2.112	2.133
170	102	106	111	2.008	2.025	2.045
214	75.6	78.0	83.1	1.878	1.892	1.919

As the graphic representation shows, the logarithm of the conductivity decreases in all three series with the time, and thus is itself an exponential function of the time. $i = i_0 10^{-\lambda' t}$, the numerical value of λ' (in the common system) if the time is reckoned in hours, from Series I. = 0.00324, from Series II. = 0.00324, and from Series III. = 0.00321. This agreement is a further proof of the

* A complicated equation for this increase of the induced activity has been worked out by Curie and Danne (*Comptes Rendus*, cxxxviii., 663) and confirmed by Duane (*ibid.*, cxi., 581).

proportionality of the emanation and the induced activity produced by it.

A second series of experiments in which the readings were taken every half hour after filling the measuring tube is shown in Table III.

Age of emanation.	Conductivity.	Logarithm.
0	345	2.537
123.5	143	2.155
168	96.2	1.983
196	75.2	1.875
241	57.5	1.739
316	31.4	1.457
363	19.5	1.284
484.5	7.7	0.886

Table III. gives the value 0.00330 for the constant λ' in the common system. The mean of all four values is thus 0.00325, and in the natural system 0.0075. The decay constant λ of radium emanation thus amounts to $0.0075 = 2.08 \times 10^{-4}$, if the time is reckoned in seconds.

Consequently, the activity of the emanation decreases to half its value in 92.6 hours = 3.86 days. This number is the mean of those given by Rutherford and Soddy, and by Curie.—*Berichte*, 1905, xxxviii., 1753.

SEPARATION OF PLATINUM AND IRIIDIUM.

By L. QUENNESSEN.

THE method I now describe gives a rapid process of separation of platinum and iridium; further, it is applicable to the treatment of the residues of wires, plates, and laboratory utensils with the view to obtaining pure reagents. I was led to this new method of separation in order to obviate the difficulties presented by certain processes and the inaccuracy of others. I will first recapitulate all the methods previously described, only briefly alluding to the parts concerning platinum and iridium, and will make in each case whatever criticism I consider necessary. It must be understood that there is no question of estimating these metals in their ores, but only of their alloys.

Berzelius was the first to suggest an analytical process for estimating the metals contained in the platinum group, with the exception of ruthenium, which only became known by the later investigations of Claus, and especially in more recent times by the remarkable researches of Joly.

After treating platinum and iridium with aqua regia, and removing the nitrous fumes with hydrochloric acid, Berzelius converted them into the chlor-platinate and chlor-iridate of potassium. These salts were dried, mixed with twice their weight of alkaline carbonate, the mixture placed in a crucible and raised to a high temperature, which finally yielded metallic platinum and the sesquioxide of iridium, insoluble in acids and aqua regia; after washing the ignited residue to remove the alkaline chlorides, a mixture of hydrochloric and nitric acid, diluted with an equal volume of water, was added, which dissolved only the platinum, the latter being precipitated from the solution by ammonium chloride.

The objection to this process is, in the first place, the large amount of alkaline salts used, and especially the difficulty experienced in removing them from the sesquioxide of iridium, which, as I shall presently show, is soluble in dilute acid.

Claus, in 1854, advised the use of sulphurous acid in order to reduce IrCl_4 to Ir_2Cl_6 , which, converted into the double chloride of ammonium or potassium, is soluble in an excess of these chlorides in solution. The drawback to this method is that, if the action of the sulphurous acid is too prolonged, it gives rise to the formation of the double sulphite, the treatment of which is laborious.

Muckle and Wöhler, in 1857, treated the chloro-platinate and chloro-iridate of potassium with potassium cyanide; they themselves knew that this method was not quantitative.

In 1867, Voldemar de Schneider treated a solution of platinum and iridium in hydrochloric acid with soda; he thus reduced the iridium chloride into sesquichloride, then into sesquioxide. On adding hydrochloric acid, he obtained in solution iridium sesquichloride and sodium chloro-platinate, and he precipitated the latter with ammonium chloride. But as the reduction by soda is never complete, the remaining iridium is re-formed by the addition of HCl into the tetrachloride, which separates with the platinum as the insoluble double salt. Further, the precipitation of the platinum is never total when the double sodium chloride is treated with ammonium chloride.

It was in 1877 that Sainte-Claire Deville and Stas, by their masterly work, effected a radical separation of platinum and iridium. This classic process consists in treating the two metals with molten lead; the platinum gives an alloy, Pt.Pb, soluble in dilute aqua regia, whilst the iridium forms no alloy with lead, and remains absolutely insoluble. This analytical method is, unfortunately, a slow one, and necessitates certain manipulations employed with success by Messrs. Matthey (London), which were communicated to Sainte-Claire Deville and Stas, but which the latter did not feel at liberty to publish.

Heraeus, in 1873, treated the alloy with aqua regia under pressure, evaporated the acid, and heated the residue to between 150° and 200° in order to transform the iridic chloride into the lower chloride.

This treatment under pressure was suggested as practically possible by Sainte-Claire Deville and Debray in 1861, by using commercial products then in use for attacking the ore. A. Quennessen had shown them that these platinum products, rich in iridium, possessed the property of insolubility when previously heated with aqua regia, which removed the greater part of the platinum of the surface alloy, a porous metallic layer being thus formed, very rich in iridium.

Iridium tetrachloride, under the conditions above mentioned, cannot be converted into sesquichloride.

Next followed the work of Seubert in 1881; after his determination of the atomic weight of platinum he employed the method given by V. de Schneider, and recognised the fact that this was nothing more than a means of purification.

Mylius and Detz, in 1899, suggested the use of hydroxylamine hydrochloride for the reduction of iridium chloride, the platinum being precipitated by ammonium chloride. IrCl₃, treated in the warm by this reducing agent, acquires a yellowish colour, not the green tint belonging to Ir₂Cl₆; as for the platinic chloride, its yellow colour becomes slightly reddish, and it is no longer precipitated by ammonium chloride. These authors, who introduced a variation of the method of Deville and Stas, have thus contributed to no improvement.

The last process is due to Leidié, in 1901. His publication is too recent for it to be necessary that I should review the mode of operation. It is the only process suitable to apply for the separation of the common metals of the platinum group—in order to effect a purification of the latter; but the method is not quantitative for platinum, iridium, nor rhodium. For it frequently happens that when the solution of the double nitrites is saturated with alkaline chloride, platinum is precipitated with rhodium and iridium, by the action of ammonium chloride, as the double nitrite of ammonia, and on treating the mixture of the salts of these metals with aqua regia, part of the platinum is precipitated and transformed into the insoluble nitrosyl salt, which will be described when the researches upon this salt are finished. I propose to operate in the following manner:—

The alloy to be analysed is treated with aqua regia of known composition: nitric acid ($D = 1.32$), 1 volume; hydrochloric acid ($D = 1.18$), 2 volumes; when solution is complete the

excess of nitric acid is first carefully removed, finally raising it to 120° in the oven, to eliminate the remainder of free acid; then water is added, and the metals precipitated from solution by magnesium. The precipitate is dried and ignited, then heated to dull redness in a current of hydrogen. After cooling the excess of magnesium is removed by sulphuric acid (diluted to one-tenth), and the residue treated with aqua regia, diluted with three times its volume of water; the platinum only dissolves, is converted into the double ammonium chloride, and ignited at the lowest temperature possible in order to avoid a sensible loss of metal in the form of PtCl₂; the use of a reducing agent is recommended, oxalic acid or glucose. The most simple means, in my opinion, consists in placing upside down in the crucible the filter containing the dried precipitate, and heating the covered crucible in the furnace; the charred paper then acts as a reducing agent, and its combustion is completed, when the operation is over, in contact with air.

In this operation I discovered that the iridium precipitated by magnesium, while still moist, is soluble in dilute sulphuric acid and in acetic acid; that it preserves this property if dried at 100°, and even at a low red heat; it is therefore probably an oxide which acquires a blue tint after drying at 100°, and whose solutions are differently coloured according to the temperature to which it has been raised.

Moist or dried at 100°, it imparts a yellow colour to dilute sulphuric acid, gradually changing to violet, and a green colour to acetic acid; it is violet with sulphuric acid if heated in air to 440°, and finally blue if raised to 800°.

I am keeping to study last of all these oxides which present such strange characteristics, contradicting what was already known of the oxides of iridium.

THORIA, THE ESTIMATION AND SEPARATION OF FROM THE YTTRIUM-CERIUM GROUP OF OXIDES.

By W. B. GILES, F.I.C.

(Concluded from p. 31).

THE solution of the cerium group of metals freed from thoria as described was then treated with an excess of sulphuretted hydrogen, and allowed to stand for twenty-four hours. The sulphide of lead was filtered off, washed, and the filtrate boiled till every trace of the hydric sulphide was expelled; the solution when cold was then made up to a volume of exactly 2 litres in a standard flask; 100.0 c.c. of the resulting solution thus equalled 2.0 grms. of the original nitrates, less the thoria which was removed. The following trials were made with this material:—(1st). In order to see whether a further treatment with a fresh supply of lead carbonate would yield any more precipitate, 100.0 c.c. were measured out, and treated with about 2 grms. more of the moist reagent with constant stirring for several hours. The precipitate was then collected on a filter, very thoroughly washed, dissolved in a little nitric acid, diluted considerably, and the lead precipitated by hydric sulphide. The sulphide of lead was filtered off, and the filtrate was evaporated to complete dryness, when only an unweighable stain was left in the basin. It was therefore seen that lead carbonate had now no action on the standard solution. (2nd). The amount of the total cerium group of oxides was determined by precipitation with only a slight excess of pure ammonium oxalate as follows:—Two portions of 100.0 c.c. were measured out into beakers, and each diluted with 100 c.c. of distilled water, raised to a boil, and then precipitated with a solution of 1.10 grms. of pure ammonium oxalate; after this the solutions were made faintly alkaline with ammonia,

and then allowed to stand for sixteen hours.* The highly crystalline precipitates were collected on ashless filters, washed, dried, and ignited over a powerful Bunsen flame till the weight remained constant.

	No. 1.	No. 2.
Cerium group oxides + crucible ..	27.6810	26.4660
Crucible	26.9065	25.6930
Grms. of ignited cerium groups oxides in 100.0 c.c. .. .	0.7745	0.7730

Or a mean percentage of 0.7737 of cerium-yttrium oxides in 100 c.c. of the solution.

Measured portions of this were then taken and mixed with the same solution of "Thorium Nitrate Absol. Chem. Pur." already mentioned (p. 2). This solution contained per 100.0 c.c., 0.4765 gm. of ignited thoria and 0.0015 gm. of other oxides not precipitable by lead carbonate, but capable of being thrown down by ammonium oxalate.

100 c.c. of the cerium oxides solution and 100 c.c. of the thorium nitrate solution were mixed, and the whole treated with lead carbonate exactly as described in the preceding pages. The thoria was after the separation of the lead thrown down by ammonia and ignited, finally over the blast-lamp. The cerium oxide group was precipitated with a solution of 1.10 gm. of pure ammonium oxalate and the oxides ignited to a constant weight over a powerful Bunsen burner.

Then 100 c.c. of thorium nitrate solution and 50 c.c. of cerium oxides solution were treated precisely in the same manner, except that only half the amount of ammonium oxalate was employed. The volume of the solutions and the amount of wash-water used was kept as uniform as was possible. The following results were obtained:—

100.0 c.c. of thoria solution—		
Thoria	Found	0.476
	Theory	0.4765
100.0 c.c. of cerium solution—		
Ceric group oxides ..	Found	0.773
	Theory	0.7752
100.0 c.c. of thoria solution—		
Thoria	Found	0.4765
	Theory	0.4765
50.0 c.c. of cerium solution—		
Ceric group oxides ..	Found	0.3885
	Theory	0.3883

These results show that a very fair separation of the oxides can be obtained by only one treatment with lead carbonate, but it is obvious that it is easy after once precipitating the thoria to re-precipitate it after removing the lead with hydric sulphide with a fresh amount of the reagent. After the thoria has been ignited it is not an easy matter to re-convert it into the nitrate. The colour of some of the ignited thoria precipitates was noted:—

	Colour.
Thorium nitrate precipitated with ammonia	Nearly white, but with a faint grey hue.
Thorium nitrate precipitated with lead carbonate ..	Almost pure white.
Thorium nitrate with 100.0 c.c. cerium solution ..	Faint brownish white.
Thorium nitrate with 50.0 c.c. cerium solution ..	Faint brownish white.

* *Solubility of the Oxalates Precipitated as described*—In view of some other experiments on these separations, it was not without interest to ascertain what was the solubility of these oxalates precipitated as described; consequently the two filtrates and washings, amounting to 550 c.c., were mixed and evaporated in a platinum dish to complete dryness. When the volume of the hot solution was reduced to about 100.0 c.c. a film of oxalates began to separate out on the surface of the liquid, and on further evaporation a decided amount separated out. The whole was evaporated to complete dryness, and then ignited till all ammonium salts were expelled and the oxalates decomposed. The small amount of brownish oxides weighed 0.008 gm., from 4 grms. of nitrates, or 100 c.c. of the solution contain about 0.08 gm. of air-dried oxalates.

It has been noted that when the same solutions are precipitated respectively with ammonia and oxalic acid, that the ignited thoria from the oxalate is always of a much lighter colour than that which is obtained from the precipitation with ammonia. All the above four precipitates had a glassy crystalline appearance. As regards the colour of the precipitate it is stated (Truchot, "Les Terres Rares," p. 196) that "Thoria obtained by the calcination of the oxalate or the sulphate gives an absolutely white powder, while that obtained by the calcination of the hydrate gives hard and transparent fragments of a greyish brown colour," and Drs. Herzfeld and Korn (in their "Chemie der Seltenen Erden," p. 131) say of ignited thoria, "Dasselbe ist weiss bis graugelt." It has been noticed that the manner in which the precipitate is ignited has a considerable influence on the final colour of the thoria. If the precipitate obtained with ammonia and dried in the air-bath at 120° C. is wrapped up in the filter-paper, and at first gently heated to char the paper and avoid projections, the resulting oxide always has a dark colour which even a long exposure to a powerful blast-lamp fails to remove entirely, while if the bulk of the dried precipitate is removed and ignited separately from the filter-paper the colour is always much lighter, and at times is almost snow-white. To clear up this doubt about the colour of ignited thoria precipitated by ammonia, fresh experiments are now being conducted on specially purified thorium nitrate.

In this connection it is well to remember that extremely small amounts of praseodymia, terbia, and possibly other members of the yttrium family, have the property of strongly colouring other oxides of the same group which, in a pure state, would give colourless oxides on ignition (Marc, CHEMICAL NEWS, vol. lxxxvi., p. 74).

Analyses of several minerals containing thoria have been made by this method. A compact mass of monasite of chocolate colour and apparently crystallised, which had a specific gravity of 5.129 and came from Arendal, yielded 8.20 per cent of thoria and a very distinct amount of uranic oxide.

Thorianite.—The writer is indebted to Prof. Wyndham R. Dunstan for a small specimen of this new and very interesting mineral, which has been examined for thoria by the lead carbonate process. The mineral was opened up by fusion with three times its own weight of sodium pyrosulphate, as the fact that it was soluble in strong nitric acid or diluted sulphuric acid was at that time unknown to him.

The following results were obtained:—

Analysis of Thorianite.		
Loss on ignition		1.92
Silica		0.70
Lead oxide		3.21
Thoria		73.94
Zirconia		0.06
Cerium group oxides		2.74
Ferric oxide		3.22
Titanic acid		traces
Uranium oxide (U ₂ O ₃)		14.18

99.97

These notes upon thoria will be supplemented by some remarks upon the separation of zirconia and ferric oxide by lead carbonate, and also by some notes upon the separation of cerium from lanthanum and didymium oxides.

Some New Dinaphthopyranic Nitrated Substances.

—A. Robyn.—When pyryl bromide reacts on aniline, ortho-, meta- and para-toluidine, and α -naphthylamine, the author obtains a number of new mono- or dipyryl-nitrated substances which are derived by elimination of the hydracid either from equal molecules of the reacting substances, or from 1 molecule of the base and 2 molecules of pyryl bromide.—*Comptes Rendus*, cxi., No. 25.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, July 10th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 227 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 227 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford during the month of June is the heaviest recorded since October, 1903; the amount actually measured was 4.15 inches. The average rainfall for the month is 2.10 inches; thus we have an excess of 2.05 inches, which cancels the previous deficit of 1.85 inches, and leaves an excess for the first six months of this year of 0.20 inch, or 1.8 per cent, on the thirty-five years' average.

Our bacteriological examinations of 395 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 787 others from special wells, standpipes, &c., making a total of 1182 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	206
New River, filtered (mean of 72 samples) ..	16
Thames, unfiltered (mean of 25 samples) ..	4493
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 198 samples) ..	38
Ditto ditto highest	242
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	264
River Lea, from the East London District clear- water wells (mean of 25 samples) ..	41
Kent District, from the wells at Deptford (mean of 25 samples) ..	1

Of the 320 daily samples taken from the general wells of the Metropolitan Water Board, fourteen samples, or 4.3 per cent, were sterile. Twenty-six samples, or 8.1 per cent, contained more than 100 microbes per c.c., and of these twelve samples contained more than 150 microbes per c.c. The twenty-six excess samples contained an average of 160 microbes per c.c. In May sixteen excess samples contained an average of 148 microbes per c.c.

It will be observed that, owing to the excess of rainfall, the microbic impurity of the raw Thames water in June has increased about four and a-half times what it was during the month of May, while the water of the Lea has been but little affected. The average of the filtered supply has also shown an increase of microbic impurity over that of the past month. This deterioration is shown by the fact that the percentage of samples containing more

than 100 microbes is nearly doubled as compared with the last month, and that twelve samples this month contain more than 150 microbes as compared with only five in the same condition in May.

The amount of organic matter in solution in the Thames-derived waters, has increased by about one-half, and their colour and the amount of oxygen absorbed is correspondingly greater. These variations we should expect from the fact that in the Thames valley during the month of June, the heaviest rainfall has been recorded since October, 1903.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES

THE FARADAY SOCIETY.

Ordinary Meeting, July 3rd, 1905.

Mr. W. R. COOPER in the Chair.

MR. SHERARD COWPER-COLES read a Paper entitled "*Some Notes on the Rapid Electro-deposition of Copper.*"

The reading of the paper was illustrated by lantern-slides, and the author exhibited specimens of copper sheets, tubes, and wire made by the "centrifugal" process.

The various processes for increasing the current densities in copper deposition by using mechanical means for keeping the copper smooth, are classified as follows:—

1. *Revolving or moving the cathode*, as in the processes of Wilde, Cotsworth, Wylie, and Grant. The current density employed is comparatively low.

2. *Burnishing the Copper during Electro-deposition (the Elmore Process)*.—The usual current density is under 20 amperes per square foot.

3. *Insulating the Growths on the Copper so as to Prevent further Increase*.—For example, the Dumoulin process in which sheepskin and other impregnators are employed. The current density is 35 to 40 amperes per square foot.

4. *Rapid Circulation of the Electrolyte*.—Examples: Thofehrn's process, in which impinging jets are caused to play on the surface of a rotating cylinder (C.D. 50 to 100); Graham's process, in which the electrolyte is discharged on to a flat cathode surface (C.D. 300, just under the influence of the jets); Poore's process, in which the solution is sprayed on to the cathode, the stream forming the only electrolytic connection; Dessolle's process, used in Paris for coppering ornamental iron work; and finally, Harrison's, likewise an impingement process. The author considers that impingement processes are not likely to be applied commercially until the amount of solution circulated can be greatly reduced.

5. *Revolving Mandrel at a Critical Speed (Centrifugal Process)*.—This process has been developed by the author, and the latest methods of working are here described. The mandrels are suspended vertically, and are provided with Pelton wheels, which are driven by the electrolyte impinging against them. In the most recent form, however, a tubular vat is used, and hollow mandrels suspended on ball bearings, through the middle of which run the spindles. These are driven by a worm gearing from below. An 8-foot mandrel has only to be driven at about fifty revolutions per minute.

The author claims the following advantages: The copper is refined and manufactured into sheets or tubes in one operation, and is of a hard nature, similar to that which is cold-rolled; the process is at least ten times faster than any existing electrolytic process; a high current can be employed without deteriorating the quality of the copper; there is no risk of lamination; the plant is simple and

free from mechanical complications; the amount of copper locked up for a given output is small compared to other processes; finally, anodes of very impure copper can be used as compared to the anode copper used in other systems.

By using a mandrel in which a V groove has been indented, the spiral deposit that results can easily be pulled away, and then drawn down at once into wire, which can thus be made from crude copper in what is practically one operation.

The estimated capital expenditure and cost of working the "centrifugal" process are given in the paper.

Mr. A. STANLEY ELMORE (communicated) said the author had not mentioned heating the electrolyte as a method of accelerating the rate of deposition. He knew of one plant working the Wilde process in which the cathode was rotated rapidly, and the current density was by no means "comparatively low." He gave some further details regarding the Elmore process. The C.D. was occasionally pushed up to 30 amperes per square foot and has been carried up to over 200 amperes. A tensile strength as high as 42 tons per square inch had been attained. By the use of a burnisher the same high C.D. could be used with a less expenditure of power than in other processes, and he claimed that by a combination of burnishing and moderate circulation of electrolyte, better and more certain results could be obtained than by the author's "centrifugal" method. He asked how the author proposed to make tubes of less than 2½ inches diameter.

Mr. MILBOURNE said that all that was claimed for the "centrifugal" process had been borne out by the results of the trials he had made with a practical plant on the Continent.

Mr. W. C. PREBBLE pointed out that in the author's process the circulation of electrolyte took place just at the place where it was most needed, namely, the surface of the cathode.

Mr. J. V. MACKENZIE described an arrangement by which he had used current densities up to 45 on electrotyping work.

Dr. C. J. STEINHART said that capital expenditure was an all-important item; whether that required in the "centrifugal" process remained within the permissible limits remained to be seen. The author had successfully surmounted the "early stage" difficulties of his process.

Mr. T. C. CLOUD criticised the author's theory regarding the growth of nodules. He thought that the toughness of the metal was the result of the particles being drawn out into long fibres as they were being deposited.

Mr. COWPER-COLES replied to the various points raised. Tubes as small as 2½ inches could not be deposited, but could easily be drawn down.

A paper on "The Use of Balanced Electrodes," by Prof. W. W. HALDANE GEE, was read in abstract by Mr. R. S. HUTTON.

The method of ascertaining the weight of metal electrolytically deposited by directly weighing the cathode in the electrolyte instead of removing the cathode and weighing it—after washing and drying—is considered. The real weight (M) is obtained from the apparent weight (m) by the formula $M = \frac{m \Delta}{\Delta - \delta}$; where Δ is the density

of the deposited metal, and δ that of the electrolyte. It is shown that since Δ occurs both in the numerator and denominator of the expression, that for most purposes it is not necessary to know the value of Δ with great accuracy. In the case of copper the value of Δ that may be used is 8.9. An ordinary physical balance is used, and a cylindrical cathode suspended by a thin wire passing through a hole in the bottom of the balance case is counterpoised in the electrolyte. The anode also is circular, and surrounds the cathode. Electrical connection is made to the cathode by a side wire whilst receiving a deposit, but is removed when the apparent increase of weight has to be ascertained. The method has been found very con-

venient in testing commercial types of ammeters. An accuracy of about 1 per cent can be generally obtained, and with a little care and by increasing the amount of deposit the accuracy can be brought under 0.5 per cent. In some experiments both sides of the balance may be used simultaneously when the electrochemical equivalents of metals in different combinations may be compared and current efficiencies ascertained. A number of experiments have been made with a mercury cathode and anode, the electrolyte being solutions of mercurous nitrate, or mercuric chloride mixed with potassium cyanide. The mercury cathode is enclosed within a shallow dish suspended in the electrolyte by a platinum wire. The anode is a layer of mercury at the bottom of the containing vessel. In the case of mercurous nitrate it is shown that the current efficiency as a monad is affected by the presence of mercuric and basic compounds. For good results the mercurous nitrate solution must be carefully prepared and a strong solution used.

Modifications of the method are described that may be used for the purpose of finding the density of electro-deposited metals, and for studying the relative loss and gain at anode and cathode.

Instead of an ordinary balance a spring balance may be substituted. The author also shows how a Nicholson's hydrometer may be used both as a cathode and as a means of finding the amount of deposit.

It is concluded that the method will be useful in the laboratory and test room as a means of rapidly arriving at results with sufficient accuracy for many commercial purposes.

Dr. F. M. PERKIN said that the drawback to the use of mercury was that only small currents could be measured therewith. What was particularly wanted was an instrument that would indicate continuously; for example, the cathode might be suspended in a helix, to which a pointer was attached, as in the Ayrton-Perry meters.

Mr. H. D. LAW and Dr. F. MOLLWO PERKIN contributed a paper on "The Electrolytic Oxidation of Hydrocarbons of the Benzene Series. Part II. Ethyl Benzene, Cumene, and Cymene." (Will be inserted in full).

Mr. H. D. LAW and Dr. F. MOLLWO PERKIN also presented a note on "The Electrolytic Analysis of Antimony."

Some little time ago, requiring to carry out a number of antimony determinations, we thought the simplest and most easy way would be to employ electrolytic methods. At first we used the method of Classen, in which the antimony salt is dissolved in sodium sulphide. This process works extremely well, and the appearance of the deposited metal leaves very little to be desired. We found afterwards, however, that the method suggested by Fischer (*Ber.*, xxxvi., 2348), in which small quantities of potassium cyanide are added to the sodium sulphide solution, yields even better results. From the point of view of accuracy of working there is no exception to be taken to the method. But the preparation of the sodium sulphide, which has to be practically saturated at the ordinary temperatures and preserved in well-stoppered bottles in a cool place, is very troublesome. We therefore endeavoured to find a method which would give accurate results, and which could be carried out at once without the trouble of preparing any special reagents.

Good results had already been obtained in this laboratory with tartrate solutions in the case of nickel, cobalt, and iron, and remembering how readily antimony salts dissolve in tartaric acid we naturally turned to it. This solution has already been tried, but apparently the results have not been found satisfactory, owing to the length of time which is supposed to be required.

In "Electrolytic Methods of Analysis," by B. Neumann, p. 145, the following remarks are made with reference to solutions in tartaric acid:—

"The electrolysis of a solution of antimonyl potassium tartrate, or of an antimony solution containing tartaric acid, yields a deposit which is entirely satisfactory; the

electrical resistances of these solutions are, however, so great (as with all other solutions containing chiefly tartrates) that the separation takes place too slowly for practical use."

We have not found solutions of tartrates to have a high electrical resistance, as will be seen from the table below. The resistance of a solution of tartaric acid is indeed rather high, owing to its slight ionisation, but that is not the case with ammonium or other alkali tartrates.

The following table shows that with hot solutions very good results can be obtained by using a solution of an antimony salt containing from 6—8 grms. of ammonium tartrate to each 120 c.c. of solution, and further, that the whole of the antimony can be deposited out in from three to five hours.

Sub- stance.	Tem- perature.	Time in hrs.	C.D. per sq. dcm.	E.M.F. Volts.	Deposit.	Per- centage Sb.	Theo- retical percent- age.
Grms.			Ampères.				
1'07624	70-80°	6	0'2-1'0	3'0-3'5	0'3882	36'08	36'16
1'07624	Cold	*	0'2-0'5	2'6-3'2	0'3902	36'26	36'16
1'07624	Cold	*	0'2-0'4	2'7-3'1	0'3890	36'16	36'16
1'07624	60-70°	4	0'2-0'6	3'0	0'3900	36'24	36'16
1'0350	65-75°	5	0'2-0'5	3'1	0'3736	36'10	36'16
1'0350	70-80°	4'5	0'3-0'8	3'0-3'4	0'3762	36'34	36'16

* Over night.

The deposits from hot solutions adhere to the cathode with great firmness. But from cold solutions, unless low-current densities are employed, the deposited metal is apt to be crystalline, or to be of a brittle nature and to exfoliate. Cold solutions, in fact, cannot be depended upon, although the appearance of the deposited metal is superior to that which is obtained from hot solutions. From hot solutions there is a tendency for the metal to have a slightly brown shade, although at times it is quite white. The addition of 1 grm. of tartaric acid to the electrolyte tends to improve the appearance of the deposit, and also prevents the tartrate solution from darkening.

In view of the trouble of preparing the sodium sulphide solutions we certainly think that this method is to be recommended, more especially as the results which we have obtained are very satisfactory from an analytical point of view.

Mr. J. H. BELCHER said that he had used the ammonium tartrate solution with success.

Mr. R. S. HUTTON and Mr. J. R. BEARD communicated some "Notes on Heat Insulation, particularly with regard to Materials used in Furnace Construction." (Will be inserted in full).

Mr. R. W. VICAREY presented a paper entitled "Storage Batteries and their Electrolytes," which was taken as read.

This is a paper intended by the author to be a *résumé* of observations and experiments referring to the deleterious effect of nitrogen compounds (especially ammonia) upon the durability, efficiency, and behaviour of storage batteries.

The paper deals with the action of ammonia and other nitrogen salts, and the salts of potassium, sodium, aluminium, magnesium, and calcium, and it discusses their uses in the various manufacturing processes. It also deals with the waters and acids used for the electrolytes of batteries.

It would appear that ammonia must be considered as a dangerous impurity, the total absence of which, however, cannot be absolutely insisted upon. The presence of ammonia in the surroundings or neighbourhood of the cell must be carefully guarded against, and the percentage actually present in the cell must be kept as low as possible by the use of waters and acids of the purest quality.

The author points out that above certain limits of ammonia little difference is observed in the behaviour of cells, but below that limit much difference occurs. Thus experiments upon cells containing proportions of ammonia varying from 10 per cent to 0.1 per cent (7040 to 70.4 grains per gallon), the loss in capacity was 22 to 31 per cent immediately after the addition of the ammonia, whilst cells containing less than 0.1 per cent did not drop in

capacity immediately, but varied intermittently from 10 to 15 per cent, finally settling at the end of eight months to a permanent loss of 15 to 22 per cent.

From the data given it appears that ammonia is very slow in its action before it makes any appreciable or apparent loss in the capacity of the cells, the average time being about twelve months, dating from the initial charge.

The effects of ammonia in its various combinations appear principally in two distinct forms: (1) it causes an excessive disintegration or shedding of active material at the positive (PbO_2) plate; (2) it becomes deposited upon the negative (spongy) plate, and finally closes up the pores of the active material, thereby causing a decrease in the ampère-hour capacity or efficiency varying from 10 to 60 per cent in about twelve months.

The use of water taken from the steam boiler and termed "distilled" is mentioned as a dangerous practice that is common in central stations, &c.

The position of the battery and its surroundings are also touched upon.

Finally, it is proposed that a series of experiments be carried out upon some cells in an attenuated atmosphere, away from all manufacturing districts.

Prof. E. WILSON presented a paper on "Alternate Current Electrolysis." This was taken as read, and the discussion postponed until the autumn.

NOTICES OF BOOKS

Précis d'Analyse Chimique Quantitative. ("Compendium of Quantitative Chemical Analysis"). By E. BARRAL. Paris: J. B. Baillière et Fils. 1905.

THIS book gives a very systematic course of analytical chemistry, and is so complete that a student who works through it, aided by a little personal direction by a teacher, should become thoroughly well grounded in the essentials of quantitative analysis. The discussion of general methods is a particularly satisfactory feature of a book which leaves little to be desired in any respect. Some organic analysis is included, methods of estimating the most important substances used in pharmacy, medicine, &c., being shortly described, though no technical analyses are contained in the book. The short account of electrolytic methods might with advantage have been somewhat enlarged, more especially as regards the manipulation and chemical details of the processes, which are not described nearly so fully as the apparatus employed, but on the whole the careful choice of the methods advocated and the succinctness and clearness of the author's language are points which win for the book a confident recommendation as an unpretentious and yet eminently useful text-book of chemical analysis.

Leçons sur la Théorie des Gaz. ("Lessons on the Theory of Gases"). By L. BOLTZMANN. Translated by A. GALLOTTI and H. BÉNARD. Part II. Paris: Gauthier-Villars. 1905.

ALTHOUGH it is now nearly ten years since the first part of Boltzmann's "Vorlesungen über Gastheorie" appeared, it still maintains its position as one of the most valuable among similar text-books, and a translation of it will no doubt be acceptable to French readers. This second part treats of the theory of Van der Waals, gases with polyatomic molecules, and the theory of dissociation, and contains a bibliography of the principal books and articles on the theory of gases which have appeared since the publication of Boltzmann's book. As in the first part valuable expository notes have been added by Professor Brillouin, of the Collège de France, and the original has lost none of its characteristic clearness and lucidity in the translation.

Transactions of the American Electrochemical Society.
Volume VI. Philadelphia: The American Electrochemical Society. 1904.

THIS volume contains the papers which were read before the Sixth General Meeting of the American Electrochemical Society, held at St. Louis in September, 1904, and also those which were read and discussed in joint sessions of Section C. of the Fifth International Electrochemical Congress and the American Electrochemical Society. Amongst the great variety of subjects treated in the book it is difficult to single out any paper as more particularly worthy of notice, especially when the general level of interest is so high, but the following must be mentioned as deserving the careful attention of all who are interested in electrochemistry, viz.:—The paper by Professor Richards, of Harvard, on "The Relation of the Hypothesis of Compressible Atoms to Electrochemistry," that by Dr. Hans Goldschmidt on "Aluminothermics," which gives an interesting account of the properties and use of "thermit," and J. Sigfrid Edström's paper on the "Electrical Extraction of Nitrogen from the Air."

shows an important difference between neodymium and the neighbouring element samarium.

A Method of Determining the Specific Heats of Solutions. Molecular Heat of Good and Bad Electrolytes.—P. Th. Muller and C. Fuchs.—Good electrolytes are distinguished from other substances in aqueous solution by a number of properties. The authors determine their specific heats by the method of electrical heating rather than by the ordinary method to avoid the considerable variation of temperature.

Researches on Mercury Formates.—Raoul Varet.—The author's experiments on mercury formates explain the rapid transformation of mercuric formate into mercurous formate, formic acid, and carbon dioxide, a reaction which evolves +53.2 cal. In the same way the decomposition of mercurous formate into liquid mercury, liquid formic acid, and gaseous carbon dioxide liberates +20.7 cal. Of the various methods of decomposition of this salt that can be imagined, this is the one corresponding to the thermic maximum.

MISCELLANEOUS.

Sir William and Lady Crookes propose leaving London at the end of July, to attend the meeting of the British Association in South Africa. They expect to return home about the middle of October, and hope correspondents and friends will consider their absence a sufficient excuse for any delay which may arise in replying to letters.

Society of Chemical Industry.—The President (Dr. W. H. Nichols) and the members of the Society of Chemical Industry of the British Empire and America, as part of the programme of their convention in London, paid a visit of inspection on Saturday to the works of Burroughs Wellcome and Co. After inspecting the "Kepler" and "Tabloid" buildings, the party was joined by a number of distinguished medical and other guests, amongst whom were Sir Patrick Manson, Lady Manson, Sir James Dick, Professor H. E. Armstrong, and Mr. R. A. Robinson, L.C.C. (President of the Pharmaceutical Society of Great Britain), and adjourned to the Wellcome Club and Institute, founded for the benefit of the firm's employees. Here luncheon was served to two thousand guests in a special marquee, after which a *fête* was held in commemoration of the completion of the firm's quarter century of work. Cablegrams of good wishes to the Society of Chemical Industry and congratulation to the firm were received from its branches and agents in Sydney, Cape Town, Milan, Constantinople, Mannheim-Waldhof, West Indies, Vienna, Berlin, Charlottenburg, Switzerland, Montreal, Calcutta, Shanghai, Persia, Amsterdam, New York, Brussels, Liège.

ST. PAUL'S SCHOOL, West Kensington.—

An EXAMINATION will be held at the above School on Tuesday, September 5th, 1904, and on the following days, for filling up about Twenty Vacancies on the Foundation.—Full particulars of the Examination can be obtained on application to the Bursar.

TO BE SOLD, the English Patent referring
to Apparatuses for Wood Impregnation (mining) applicable to Tar Distillation and Founding, &c. Thirty-six installations have been started in Germany, with large profits.—For particulars address, in German, "K.D. 3573," Rudolf Mosse, Cologne.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 25, June 19, 1905.

Preparation and Properties of Azotyl Fluoride.—Henri Moissan and Paul Lebeau.—The authors show that fluorine does not act on nitrous oxide and nitrogen peroxide at ordinary temperatures, and that a new gaseous compound, azotyl fluoride NO_2F , is produced with nitric oxide. This gas has density 2.24. Its fusion-point is -139° and its boiling-point -63.5° . It possesses great chemical activity. It does not, however, combine at ordinary temperatures with hydrogen, sulphur, and carbon, but unites with boron, silicon, phosphorus, arsenic, antimony, and iodine. It decomposes cold water with production of hydrofluoric and nitric acids, and it reacts on a large number of organic compounds, and in all these reactions it acts by its own fluorine and the group NO_2 .

Alcyl Thuyones and Compounds of Thuyone with Aromatic Aldehydes.—A. Haller.—Thuyone contains a

complex $\begin{array}{c} \text{CO} \\ | \\ \text{CH}_2 \end{array}$, in which the group CH_2 lends itself to

substitutions analogous to those which the author obtained with menthone and methylhexanone, and also to condensations with the aromatic aldehydes. The thuyone used for the preparation of the various derivatives distilled at 84° under 13 m.m. pressure, was of density 0.9206, and had rotatory power $[\alpha]_D = +74.30^\circ$.

A Basic Ferric Sulphate.—A. Recoura.—During his researches on ferric sulphate the author isolated a basic sulphate whose composition is interesting because it throws light on the constitution of the hydrated ferric salts. This basic salt plays an important part in the phenomena which take place in solutions of ferric sulphate during their evaporation for the isolation of this hydrated sulphate. When obtained pure it is in the form of a yellowish white powder very soluble in water, and having the composition $6[\text{Fe}_2\text{O}_3, 3\text{SO}_3], \text{Fe}_2\text{O}_3$.

Chemical Properties of the Anhydrous Chloride of Neodymium.—Camille Matignon.—A systematic investigation of the chemical properties of neodymium chloride leads to the preparation of a crystalline oxychloride by two distinct methods in the same manner as in the preparation of the bromide and iodide of anhydrous neodymia. The action of hydrogen on this compound

TABLE OF RARE ELEMENTS.

By E. L. N. ARMBRECHT.

Symbols, Atomic Weight, Discoverer, Isolater, Specific Gravity, Principal Source, Melting-point, Properties, Salts of, Price, &c.,

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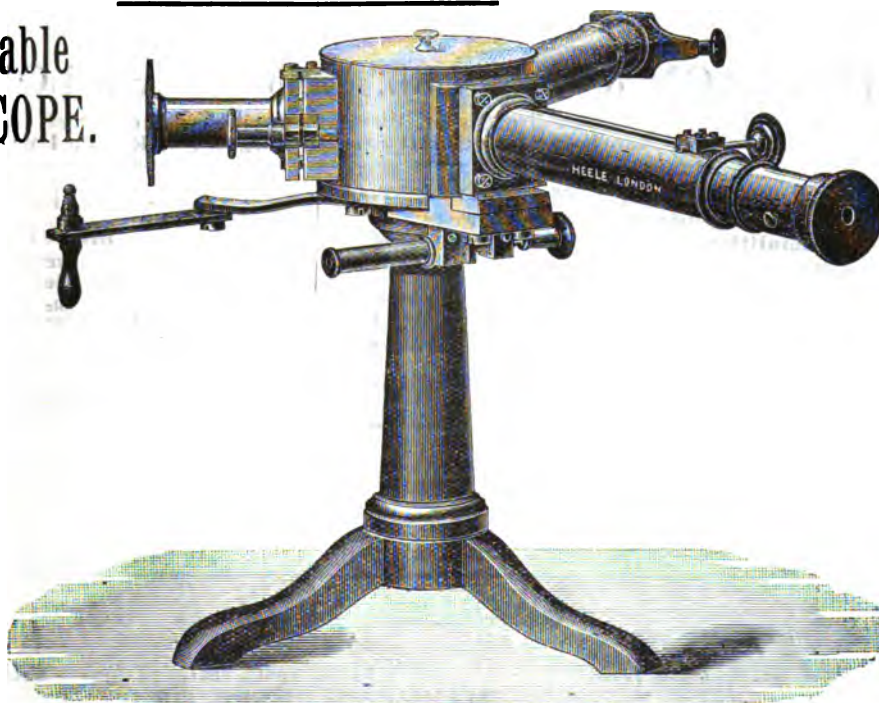
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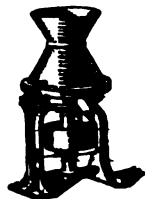
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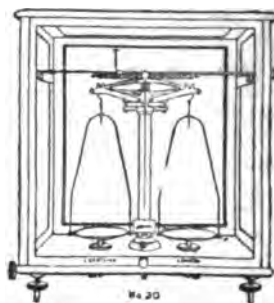
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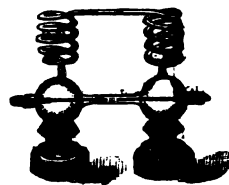
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COLOURS IN METAL GLASSES, IN METALLIC FILMS, AND IN METALLIC SOLUTIONS.*

By J. C. MAXWELL GARNETT.

In the first section of this paper it is pointed out that one and the same metal may cause a great variety of different colours, just as the colour of gold vapour differs from the colour of the light reflected from gold as well as from the colour of the light transmitted by gold leaf. While the ultimate cause of the colour of a metalliferous medium is to be found in the structure of the metal molecule itself, the arrangement of these molecules, according to any fixed law, causes them to affect one another's free periods in a definite manner, and thus gives rise to corresponding optical properties. The object of this paper is to discover, by means of these optical properties, the molecular arrangement (microstructure) of various metal glasses, of colloidal solutions of metal, and of metallic films.

Expressions giving the refractive index and the absorption coefficient (the optical constants) of a compound medium consisting of metal (1) in small spheres (granular), and (2) in discrete molecules (amorphous), diffused through an isotropic non-dispersive transparent medium (the solvent), are next investigated in terms of the corresponding optical constants of the normal metal.

The particular formulæ which apply when the volume proportion of metal in the compound medium is small, as in the case of metal glasses and of "colloidal solutions" of metal in water, are also obtained, and it is found that while spheres of any metal, so diffused that there are many to a wave-length of light, will produce colours which vary with the refractive index of the solvent, diffused molecules of any metal produce, by transmitted light, a colour (the vapour colour) which is independent of that refractive index.

By means of these formulæ and of the optical constants of gold, silver, and copper, experimentally determined for monochromatic light of several different wave-lengths, the numerical values of the corresponding optical constant which would be possessed by diffusions of spheres and of molecules in glass, water, or vacuum, are calculated and tabulated. Defining the absorption of light of wave-length λ by any absorbing medium as being the logarithm of the ratio of the intensities of that light before and after traversing a unit-length of the medium, graphs are given of the calculated absorptions of these diffusions. Curves are also shown representing the absorptions of specimens of gold ruby glass, of silver stained glass, and of copper ruby glass, as measured at the National Physical Laboratory.

A comparison of these curves with the graphs for gold spheres and for gold molecules in glass, and a collation of the results with others already obtained in a previous communication (*Phil. Trans.*, A, 1904, pp. 385 to 420), leads to the conclusion that the colour of gold ruby glass is due primarily to the presence of small spheres of gold. The irregular blue and purple colours sometimes exhibited by gold glass are then explained by the presence of crystallites caused by the coagulation of the gold spheres. Again, when the corresponding graphs with water as solvent are compared with the absorptions of colloidal gold as measured by Felix Ehrenhaft (*Ann. der Phys.*, 1903, vol. xi., p. 489), little doubt remains but that colloidal gold consists of small spheres in suspension; the blue colour produced by particles coarser than the small spheres is, as

in the case of glass, due to the red light being reflected by the crystallites and so not transmitted.

The close similarity between the observed absorptions of yellow glass stained with silver, and the calculated absorptions of a diffusion of silver spheres in glass—the calculated absorptions of a diffusion of silver molecules in glass are quite different—indicates that the stained region must contain small spheres of silver. Ehrenhaft's description (*loc. cit.*, p. 507) of the nature and position of the absorption band observed in the spectrum of colloidal solutions of silver, describes so well the position of the absorption band determined by calculation for a diffusion of silver spheres (but not of silver molecules) in water, as to justify the conclusion that the bulk of the silver present in colloidal solution is in the form of small spheres: little if any being in true solution (*i.e.*, molecularly subdivided); and this conclusion is confirmed by the fact that the refractive index of a colloidal solution of silver, which was measured by Barus and Schneider (*Zeit. f. Phys. Chem.*, vol. viii., p. 278), is precisely that which calculation shows to be possessed by a diffusion of silver spheres (but not of molecules) in water.

Measurements, made by Sir William Abney, of the intensities with which light of various wave-lengths is reflected from the interface between the stained and unstained regions of one of the specimens of silver glass which had belonged to Stokes, when held with the stain turned away from the source of light, are in general accordance with the reflective powers calculated on the hypothesis that small spheres of silver are distributed throughout the stained regions, the maxima corresponding to light of wave-length about $\lambda = 0.436$ in both cases. If the silver in the glass had been molecularly subdivided the maximum would have been at about $\lambda = 0.360$. The presence of silver spheres (but not of discrete molecules of silver) throughout the stained region thus accounts for the blue reflection, in accordance with Stokes ("On the Change of Refrangibility of Light," *Phil. Trans.*, 1852; "Collected Papers," vol. iii., p. 316), as well as for the amber colour of silver glass viewed by transmitted light, proving that both colours were due to suspended particles of silver.

A comparison of the observed absorptions of copper ruby glass with the calculated absorptions of copper spheres and of copper molecules diffused in glass, shows that copper ruby glass owes its colour to the presence in the glass of small spheres of metallic copper,* while some copper molecules are probably also present. Although it has thus been proved that gold and copper ruby glasses and silver glass owe their colours to diffused spheres of the metal, the metals which colour some other glasses cannot be present in the metallic form; for example, the deep blue colour of cobalt glass cannot be due to diffused metallic cobalt, which, according to calculation, would give a reddish colour by transmitted light akin to that observed by Ehrenhaft (*loc. cit.*, p. 506) in a "colloidal solution" of that metal.

The colours produced in gold, silver, and soda glasses by the radiation from the emanation from radium, give rise to the suggestion that all glasses contain free ions of metal, and it is by the discharge of these ions and the consequent reduction of the metal (so that the metal is diffused in the glass), that cathode and Becquerel rays are able to colour the glasses.

Expressions are obtained giving the absorptions and reflective powers of amorphous or granular forms of gold and silver, the specific gravity of which is any proper fraction, μ , of that of the metal in its normal state. Curves are constructed to show how the values of these expressions, and thus also the colours exhibited by transmitted and by reflected light, vary with μ .

A comparison of these calculated colour changes with those actually shown by gold and silver films, such as those deposited on glass by Faraday (Bakerian Lecture, *Phil.*

* Stokes (*loc. cit.*, vol. iv., p. 245) thought copper ruby glass was coloured by suboxide of copper, and attributed the change of colour in some specimens to suspended particles of the metal.

* Abstract of a Paper read before the Royal Society, June 8, 1905.

Trans., 1857), and by Beilby (Hurter Memorial Lecture, Glasgow, 1897), when subjected to heat and to pressure, indicates that (a) the films as first prepared are in the amorphous or granular phase, and (b) heating diminishes the density of the film, while pressure is able to increase that density again, and finally (c) this diminution of density is probably effected by the passage of metal from the amorphous to the granular phase, and by the growth of the larger granules at the expense of the smaller, while increase of density is accomplished by changing some of the metal from the granular to the amorphous phase.

The optical properties of Carey Lea's (*Amer. Journ. Science*, 1889, and *Phil. Mag.*, 1891) so-called solutions of allotropic silver show that they consist of small spheres of silver in suspension in water. From this and other evidence it is shown that the suggestions made in the former paper (*loc. cit.*, p. 419) that Carey Lea's silver was not allotropic, but consisted of normal silver in a finely divided (but not necessarily granular) state, was almost certainly correct.

The three forms of silver discovered so long ago as 1861 by Hermann Vogel (*Pogg. Ann.*, 1861, vol. cxvii., p. 316), were probably the amorphous, granular, and crystalline forms discussed in this paper.

The paper concludes with the suggestion that many forms of metals which have hitherto been considered to be allotropic, because possessing optical properties distinct from those belonging to the metal in its normal state, are merely cases of fine division. Thus the properties of Bolley's lead (*cf.* Roberts Austen, "Metallurgy," p. 90), of Schützenberger's (*Bull. Soc. Chim.*, 1878, vol. xxx., p. 3) silver and copper, and of other alleged cases of allotropy cited by Roberts Austen (*loc. cit.*), do not require the postulation of an allotropic molecule for their explanation.

ACTION OF AMMONIA AND OXIDISING AGENTS ON METALS.

By Dr. HODGKINSON and A. H. COOTE.

In the *British Association Report*, Section B, Cambridge Meeting, 1904, we read a short note on the "Action of Ammonium Nitrate on some Metals."

As it appeared to be to some extent a case of oxidation of the metal at the expense of the nitric oxygen and the solution of the metallic oxide, or hydroxide, in ammonia, we have, since publishing that note, made a number of experiments with other oxidising substances than the oxygen of the NO_3 group in the presence of considerable amounts of ammonium hydroxide.

It occurred to us that the simplest oxidising substance we could employ would be hydrogen peroxide. Many metals are most vigorously attacked by hydrogen peroxide under ordinary conditions. The case of iron is well known.

In one set of experiments we have employed hydrogen peroxide (commercial 20 vols.) mixed with an equal volume of 0.8800 ammonia solution. In this we have immersed weighed amounts of metals for a definite time, and of approximately the same area. As in the case of the ammonium nitrate experiments, we commenced with cadmium. Our results at present are expressed in percentage loss in a definite time—five minutes in this case.

Cadmium, 32 sq. c.m., 1.795 grms. Lost 7 per cent.
Copper, 30 sq. c.m., 7.64 grms. Lost 1.4 per cent.
Copper (2), 32 sq. c.m., 1.37 grms. Lost 3.6 per cent.
Iron. Absolutely no action.
Zinc, 32 sq. c.m., 1.79 grms. Lost 3.9 per cent.
Copper-nickel alloy, 32 sq. c.m., 13.51 grms. Lost (about) 0.1 per cent.

We also give two results with cadmium and copper-nickel in a solution of ammonium nitrate to which ammonium hydroxide and hydrogen peroxide was added.

Cadmium, 32 sq. c.m., 1.672 grms. Lost 18 per cent.
Copper-nickel, 32 sq. c.m., 13.51 grms. Lost 1.0 per cent.

The much increased action of the ammonium nitrate solution, to which hydrogen peroxide had been added, on metals is perhaps explicable. When metals dissolve in ammonium nitrate solution alone we have shown that nitrites are formed (*British Association*, 1904). When hydrogen peroxide is present a nitrite does not appear to be formed. In fact a sodium nitrite solution, to which ammonia and hydrogen peroxide were added, did not give the α -naphthylamine sulphanilic acid test for nitrous acid.

THE RELATIVE PROPORTION OF RADIUM AND URANIUM IN RADIO-ACTIVE MINERALS.

By E. RUTHERFORD and B. B. BOLTWOOD.

THE experiments made by one of us (Boltwood, *Phil. Mag.*, 1905, [6], ix., 599), have shown that within the limit of experimental error the amount of radium present in radio-active minerals is proportional to the content of uranium. The amount of radium corresponding to each gm. of uranium in a mineral is thus a definite constant which is of considerable practical as well as theoretical importance.

The proportionality between the content of uranium and radium in radio-active minerals strongly supports the view that radium is a decomposition product of uranium. According to the disintegration theory, the amount of radium per gm. of uranium present in a mineral should be a constant whose value can be approximately deduced if the relative activity of pure radium and pure uranium is known.

In order to determine the amount of radium associated with one gm. of uranium it is only necessary to compare the activity of the emanation produced by a standard quantity of pure radium bromide with that produced by a quantity of mineral containing a known weight of uranium.

In the experiments which are to be described, a standard solution of radium bromide was prepared from a specimen of radium bromide, which had been found experimentally by Rutherford and Barnes to give out heat at a slightly greater rate than 100 gm.-calories per hour. The radium bromide was, therefore, probably pure. About 1 m.grm. of the salt was taken and weighed as accurately as possible on a balance. The weighing was confirmed by comparing the relative gamma-ray effect produced on an electroscope by the sample in question and the effect produced by a quantity of radium bromide weighing 23.7 m.grms. The determinations by the two methods were found in good agreement.

The known weight of radium bromide was dissolved in water and solutions were successively made up which contained 10^{-8} and 10^{-4} m.grm. of radium bromide per cubic centimetre. Of the more dilute solution a quantity equivalent to 1.584 c.c. was carefully weighed out, transferred to a glass bulb having a capacity of about 100 c.c., and diluted to a volume of about 50 c.c. with pure distilled water. The bulb was sealed and allowed to stand for about sixty days in order that the maximum quantity of emanation might accumulate. At the end of this period the emanation was completely removed by boiling the solution and was transferred to an air-tight electroscope, in which its activity was measured. The observed activity corresponded to the emanation from 1.584×10^{-4} m.grm. of radium bromide, which was assumed to be equivalent to 0.926×10^{-4} m.grm. of radium.

The activity of the maximum or equilibrium quantity of emanation produced by the radium associated with 1 gm. of uranium in a radio-active mineral was determined by the method which has already been described (Boltwood, *loc. cit.*). The mineral chosen was a very pure sample of uraninite from Spruce Pine, N.C., containing 74.65 per cent of uranium.

The activity of the emanation from the standard radium bromide solution was equal to 24.24 divisions per minute. The activity of the emanation from 0.1 gm. of the mineral was equal to 14.45 divisions per minute, corresponding to 193.6 divisions per minute for each gm. of uranium present. These values indicate that the quantity of radium associated with 1 gm. of uranium in a radio-active mineral is equal to approximately 7.4×10^{-1} gm. One part of radium is therefore in radio-active equilibrium with approximately 1,350,000 parts of uranium.

By the application of these numbers to the ordinary ores of uranium it is possible to determine their actual content of radium. Thus a high-grade pitchblende ore containing 60 per cent of uranium carries approximately 0.40 gm. of radium, equivalent to 0.69 gm. of radium bromide, per ton of 2000 pounds. A low-grade 10 per cent uranium ore will contain per ton approximately 0.067 gm. of radium, equivalent to 115 m.grms. of radium bromide.

The amount of radium occurring with uranium is about the amount to be expected if uranium is the parent of radium, but a satisfactory comparison of theory with experiment is not possible until the relative activity of pure radium and pure uranium is more accurately determined. Experiments in this direction are in progress and the results will be given in a later paper. A method has been devised for determining in a radio-active mineral the proportion of the total activity due to the presence of uranium, radium, and the other radio-active bodies. The results obtained lead to the conclusion that actinium is not a direct product of uranium in the same sense as is radium. An account of these experiments will be published later.—*American Journal of Science*, xx., No. 115.

PRELIMINARY OBSERVATIONS ON RADIO-ACTIVITY AND THE OCCURRENCE OF RADIUM IN AUSTRALIAN MINERALS.*

By D. MAWSON, B.E., Junior Demonstrator in Chemistry,
and
T. H. LABY, Acting-Demonstrator in Chemistry in the
University of Sydney.

Literature.

PROFESSOR H. BECQUEREL, as is well known, was the first to observe what is now called radio-activity in uranyl-potassium sulphate. Schmidt extended the observations to thorium minerals (*Wied. Annal.*, 1898, lxx., p. 141). Madame Curie (*Comptes Rendus*, 1898, cxxvii., p. 1601), who independently made the same discovery, has published values of the radio-activity of thirteen minerals (Thesis présentée à la Faculté des Sciences de l'Université de Paris) of high uranium and thorium content, as measured by the ionisation produced in an air gap. Sir W. Crookes (*Proc. Roy. Soc.*, 1900, lxxvi., p. 409) looked for radio-activity by a photographic method in his collection of minerals, especially among the barium ones; but found only euxenite, alvite, arrhenite, sipilite, and hiebnite to be active. These minerals contain either uranium or thorium. No instance of the comparatively intense activity of minerals containing these elements has been found in their absence. The Hon. R. J. Strutt (*Proc. Roy. Soc.*, 1904, lxxiii., p. 193) examined the activity of samarskite, fergusonite, pitchblende, malacone, monazites, and zircon by a different method, depending on the rate of decay of the activity of the gas given off when the minerals were heated.

American uranium bearing minerals were examined by B. B. Boltwood (*Am. Journ. Sci.*, 1904, xlviii., p. 97) for radium, and it was found that in uraninite, gummite, uranophane, and samarskite, the radium present as indicated by the emanation method was proportional to the

uranium content. This does not appear to hold, for the uraninite and samarskite examined by Strutt for the former was only half as active as the latter, and this would scarcely be the ratio of the uranium in the two minerals. More recently (*loc. cit.*, p. 378) he has studied the radio-activity of natural waters. Radium has been found by Obalski (*Eng. and Min. Journ.*, March 17, 1904) to occur in a cleveite and in a bituminous substance from Quebec, containing uranium as an impurity. Elster and Geitel (*Phys. Zeit.*, 1903, v., p. 11) have detected radio-activity in fine mud from the Italian watering place Battaglia. Radio-activity was detected in natural gas by E. F. Burton (University of Toronto Studies—Physical Science Studies). An examination of the radio-activity of Russian muds was made by J. Borgmann (*Nature*, 1904, lxx., p. 80). A radio-active gas was found in the soil and water near New Haven, U.S.A., by H. A. Bumstead and L. P. Wheeler (*Am. Journ. Sci.*, 1903, xvi., p. 328, and 1904, xvii., p. 97). Later Mr. Bumstead published an account of atmospheric radio-activity (*loc. cit.*, xviii., p. 1).

M. F. Pisani (*Bull. Soc. Franc. de Minéralogie*, 1904, Part I., xxvii., p. 58) has recently examined by photographic methods a large number of diverse types of minerals, in all about 77, and found that in every case those containing uranium or thorium were active; exceptional cases were certain specimens of fluor spar, which from his results appear to act comparatively strongly on the photographic plate. Specimens of fluor spar from the same districts were tested in our apparatus, and gave negative results. M. G. Bardet (*Bull. Soc. Franc. de Minéralogie*, 1904, Part I., xxvii., p. 63) arranges a number of the more common uranium and thorium minerals in a comparative table, according to the activity exhibited photographically. R. W. Brocke (*Eng. and Mining Journ.*, June 2, 1904) has published a comparative table of activities measured by a simple type of electroscope.

Experimental Methods.

A preliminary examination of a number of the minerals was made photographically, and the active ones were readily detected. No disagreement was found between the photographic and the electrical methods. Since the β - and γ -rays are the photographically active ones, it is an unsafe method, as Rutherford has pointed out, to rely on alone. Our results, as stated in the table, were obtained by the use of a C. T. R. Wilson's electroscope (*Proc. Camb. Phil. Soc.*, 1903, Part II., xii.), consisting of a rectangular brass box, with a narrow gold leaf, insulated throughout with sulphur, and made by one of us in the Engineering Laboratory. The plate potential used was about 209 volts (as measured by a static voltmeter of the Physics Department), which gave the maximum sensitiveness. The case was preserved throughout at a constant sensitive angle of tilt. The movement of the gold-leaf was read by means of a microscope moved by a screw thread. The leaf was connected to the upper of two insulated brass plates 11 c.m. in diameter separated by a 5 c.m. air gap, and surrounded by a metal case which was earthed. The lower of the plates was kept at a positive potential of 300 volts, by means of a battery of test-tube accumulators, which was found sufficient to produce a saturation current. On this plate the mineral was placed in a circular lead dish of 5 c.m. diameter, 3 m.m. in depth—a fresh one being used for each mineral.

As Madame Curie found that the activity of uranium oxide U_2O_5 was constant for a period of five years, we compared the current passing when the mineral was tested with that from uranium oxide, the same standard specimen being used for each comparison. This was done by observing the time with a stop-clock, when the leaf took to fall through the same distance, first with the mineral then with the U_2O_5 . In all cases the minerals were finely ground, and the lead dish completely filled and levelled off.

In examining the emanation from several specially selected minerals, about 40 grms. of the finely powdered substance was heated in a porcelain tube in an organic

* Read before the Royal Society of N. S. Wales, October 5, 1904. From the *Journal and Proceedings of the Royal Society of N. S. Wales*, vol. xxxviii.

combustion furnace to the highest attainable temperature. The tube was pumped out whilst thus heated, allowed to fill, and air drawn over from the other end, and again pumped out. The gas from the Sprengel pump was collected over mercury, and transferred to a partially evacuated metal vessel, of about 800 c.c. capacity, with a central insulated wire. The gas in the vessel was brought to atmospheric pressure by the addition of air. The walls of the vessel were kept at a positive potential of 300 volts, and the current through the gas to the wire, attached to the gold leaf of the Wilson electroscope, charged it positively with resulting fall of the leaf.

Measurements were taken over a period of four days and the results plotted. Decay of the radio-activity of the emanation to half its initial value in four days indicates, as shown by Rutherford and Soddy, the presence of radium. Our instrument was not suited for measuring the decay of the thorium emanation. In this work Rutherford's "Radio-activity" was found most useful, especially the chapter on methods of measurement.

Results.

A large collection of minerals was examined, and as expected, only those containing uranium or thorium were found to have measurable activity. The apparatus readily detected an activity of $\frac{1}{18}$ that of U_2O_5 . Among the minerals tested and found to be inactive the following are worthy of mention:—

Columbite, Barrier Ranges, N.S.W.	} Various localities.
Stibiotantalite, Greenbushes Tin-field, W.A.	
Zircons	
Tellurides	
Bismuth ores	
Tin stones	
Barytes	

As will be noticed in referring to the following table, only two occurrences of uranium minerals have been recorded, so far as we are aware, in Australia. In both cases specimens at hand, up to the present time, are too small to admit of complete investigation. The first is a *euxenite* occurring with stream tin at the Marble Bar Tin-fields, W.A., and is derived from the degradation of Pre-Cambrian gneiss. The other specimen is a *torbernite* occurring in small flakes adhering to decomposed eruptive rock of intermediate character, and was collected by one of the officers of the Mines Department at the cobalt mine Carcoar (*Records Mines Dept. N.S.W.*, vol. iv., p. 20). The association of cobalt and uranium ores at Joachimsthal in the Bohemian Erzgebirge at Schneeberg, in Germany, and occurrence of slightly radio-active silver cobalt ores at Temiscamingue in Canada has already been remarked by R. W. Brock (*loc. cit.*). This circumstance, however, is regarded by the authors as accidental.

The Australian minerals whose activities have been recorded in the table are with one exception monazites. These *monazites* frequently occur in the tin fields throughout Australia, and on account of their thoria contents have lately become of commercial importance. Monazites are found to a less extent *in situ*, at Torrington in a decomposed granite, and at Warialda embedded in a lode of bismuth carbonate.

New South Wales varieties are of a hyacinth colour, well crystallised, and exhibit two good cleavages. (See *Annual Report Dept. Mines N.S.W.*, 1903; and *Records of Australian Museum*, 1903). The Pilbarra *monazite* in which we have identified the presence of radium (*vide postea*) is darker in colour than the N.S.W. specimens, and cleavages are not so well defined. It is found in the tin wash in association with *euxenite* and *gadolinite*. It will be noticed in referring to the figures in the table that no relation can be traced between radio-activity and thoria contents. This points to the presence of some other active substance in addition to the thoria.

The *gadolinite* from the Cooglegong River, W.A., was collected by Mr. B. F. Davis, B.Sc., and is described as

Total Activity as Determined by Ionisation Produced in Air-gap.

Mineral.	Activity.	Locality, &c.
Black oxide of uranium, U_2O_5	100	Taken as standard.
Torbernite	Highly active	Carcoar, N.S.W. (insufficient for comparative test).
Euxenite	Highly active	Marble Bar Tin-fields, W.A. (insufficient comp. test).
Gadolinite	0.88	Cooglegong River — Greenbushes Tin-field, W.A.
Monazite	11.30	Pilbarra, W.A.
Fine river sand with gold, tinstone, &c. . . .	8.49	Tumbarumba, N. S. Wales.
Zircon sand with monazite	0.60	Tooloon River, N. S. Wales. Contains 0.45 per cent thoria.
Concentrated beach sand	7.39	Broken Head, Richmond River, N.S.W.
Ditto, ditto	1.82	Ballina, Richmond River, N.S.W. 2R
Concentrated river sand..	8.00	Tasmania.
Monazite	5.47	Torrington, N.S.W. A large well developed crystal used.
Ditto	3.25	Torrington, N.S.W.
Ditto	4.92	Cow Flat, Torrington, N.S.W., contains 0.3 per cent thoria.
Ditto	3.11	20 miles W. of Torrington, contains 1.5 per cent thoria.
Ditto	4.46	Ditto, contains 1.8 per cent thoria.
Ditto	3.31	} Various samples from the Gulf Mine, Emma-villa.
Ditto	3.00	
Ditto	3.41	
Ditto	3.13	
Ditto	2.50	Contains 0.6 per cent thoria
Ditto	4.50	Paradise Creek, Emma-villa, N.S.W.
Foreign Minerals.		
Pitchblende	354.05	Joachimsthal. } Given for comparison.
Samarskite	47.10	Sweden
Thallium blende . . .	3.75	Locality unknown. Activity may be due to the probable association of uranium minerals.

occurring both with the stream tin in alluvial deposits and in lode formations in Pre-Cambrian gneiss (*Journ. Roy. Soc. N.S. Wales*, 1902, p. 286). In the paper cited an analysis is given, and it is stated that Prof. Norman Collie found 1 bubble of helium in the gases obtained by heating 10 grms. of the mineral. This is the first authentic case in which radio-activity has been noticed in *gadolinite*.

Examination for Radium.

The method adopted was that used by Hon. R. J. Strutt depending on the decay of the emanation. A preliminary experiment was conducted on 5 grms. of carnotite* from Colorado, U.S.A. Its emanation was found to be strongly active, the rate of decay determining it to be due to radium. Three Australian minerals were next tested with the following results:—

* Since then B. B. Boltwood has published that radium emanation is obtained from this mineral.—*Am. Journ. Sci.*, 1904, xviii., p. 97.

Gadolinite from West Australia (38 grms. tested) gave no radium emanation. In view of the fact that helium is intimately related to radium, this result is extremely interesting, as the gadolinite has been shown to contain helium (*vide ante*). A similar instance is that of a meteorite from Virginia, examined by Strutt (*Proc. Roy. Soc.*, 1904, lxiii., p. 193). In this case, although the presence of helium was detected by analysis, the meteorite failed to give the radium emanation. In the gadolinite, although thorium is not mentioned in the statement of analysis, later investigation by Acting Professor Schofield showed that a small percentage is present, and the activity is probably referable to this.

Pilbarra monasite (31 grms. tested) gave a definite radium emanation decaying to a half in very slightly under four days. The value of the radium activity cannot yet be assigned until more comparative data are obtainable.

Monasite from Paradise Creek, Emmaville, N.S.W. (25 grms. tested) gave an emanation decaying in a very short time, and not measurable with our apparatus.

Summary.

A number of Australian minerals have been examined for radio-activity by the ionisation produced in an air gap as measured by the most recent form of a C. T. R. Wilson electro-scope. The activities are compared with that of black oxide of uranium. Radium was tested for in four of the minerals by heating them in a vacuum, and testing the rate of decay of the radio-activity of the resulting gas.

A gadolinite in which Prof. Norman Collie found helium to be present was radio-active, but no radium emanation could be detected. A number of monazites were radio-active, one from Pilbarra, W.A., gave the radium emanation. It is intended to continue this work shortly, when all results will be published in ampères.

For the suggestion of the research, carried out in the Chemical Laboratory, and for constant encouragement we wish to thank Prof. David. We are indebted to the Department of Mines for a number of minerals, and especially to Mr. G. W. Card, A.R.S.M., for his cordial help in obtaining us specimens. Our thanks are also due to Acting Professors Schofield and Knibbs for encouragement and interest shown in the research.

SOME RESULTS OF LATE MINERAL RESEARCH IN LLANO COUNTY, TEXAS.

By WILLIAM E. HIDDEN.

THE noted gadolinite locality in Llano County, Texas, known as Barringer Hill, was re-opened* and thoroughly prospected by the writer, during the winter of 1902-3, with very encouraging results. All the old cuts were cleaned out and extended, and a systematic development of the mine was begun at the south-east point of the hill, and at as low a level as the river terrace would permit. The plan was to remove the hill by blasting, and gradually make a dump of it towards the near-by Colorado river. The season proved to be a very propitious one, and much good work was accomplished. Seven years had elapsed since any work had been done upon the property, but in a short time all the old familiar minerals had been re-discovered either in new openings or in extensions of the original workings of Mr. Barringer.

Among the most notable discoveries of "Barringer Hill" minerals, at this time, were the double crystal of gadolinite that weighed seventy-three pounds and an eighteen-pound mass of yttrialite; a mass of pure allanite that weighed over three hundred pounds; about fifty pounds of thorogummite, among which were pieces weighing fully a pound and some few good crystals. Of fergusonite several very

pure masses and large aggregations of rough crystals were found, up to five pounds in weight. Of rowlandite one very pure mass weighing just one kilo. was obtained; of nivenite and mackintoshite very little was discovered. The mineral species rich in yttrium-erbium were more particularly sought after because thorium and uranium were not used in the "glower" of the Nernst lamp.

Masses of coarsely crystallised fluorite up to four hundred pounds weight were not rare, and some of these had very large faces of the cube and rhombic dodecahedron. Its colour varied from dark green to puce and purple, and colourless transparent rough crystals having remarkably perfect cleavage were sometimes observed. Some of the fluorite was true chlorophane and exhibited a brilliant green light when strongly heated and viewed in the dark. One mass was self-luminous, at night, without heating it. Enormous crystals of orthoclase were common, some over five feet in diameter. Quite frequently small veins of very perfect red felspar crystals (highly-twinned), and upon which albite crystals were attached, were found bordering the fluorite and penetrating it. In the felspar, well crystallised menaccanite was sometimes observed, and this mineral is new to the locality. Yellow rutile, of the sagenitic variety, was observed in only one instance and then upon smoky quartz crystals. Polycrase, or an allied species, was seen implanted upon the gadolinite; this is also new to the region. A cavity into which a horse could have been put was discovered on the river side of the mine, and from it a large crystal of smoky quartz was taken that weighed over six hundred pounds. It was forty-three inches high and twenty-eight inches broad, and fifteen inches thick. This is now in the University of Texas collection at Austin, Texas.

Very fair amethysts were found in the west end of the hill, in cavities in the felspar. Masses of biotite, four feet across, were met with and always indicated the presence near by of the rare-earth minerals. Some of the fluorite contained small thin veins of a very dark mineral, which was deep indigo-purple by transmitted light, and this may, perhaps, betoken the occurrence of a basic fluoride of the yttrium or cerium earths at this mine and in the region generally.

In a period of four months there was taken out of the hill enough of the yttrium ores to suffice for the Company's needs for the balance of the year, and the mine was therefore closed for the season.

In the following winter (1903-4) the work was again resumed at Barringer Hill, and about a dozen workmen were kept constantly employed for a period of six months. The scheme of development laid down by the writer in 1902 was carried forward with much energy. Considerable "dead-work" was done in the line of removing "topping" and bringing up the "fall" from the river-side of the hill. New cuts were opened, and the whole top of the hill was blasted away. All the work done at the mine thus far has been of the character of open quarry work, with hand-drilling and the use of powder and dynamite. The mine has been proved to have a deep-seated origin and is only one of a series of so-called "blow-outs" in a region that is entirely granitic. Deep work at this locality may be expected to bring to light new combinations of the rare earths and of uranium and of thorium, as well as great quantities of the species for which the hill is already famous. All the old species will probably be found in a purer state and perhaps in their normal condition as when first crystallised. This last mentioned condition is what we are eagerly seeking for in order to clear up the formulæ of many of the species.

During last winter's work all the old minerals, excepting rowlandite, were again found and more than one thousand pounds of very pure gadolinite. The seventy-three pound group of crystals (of gadolinite), found in March, 1903, was the greatest "find" of record in this mineral; but just one year later, a mass of roughly crystallised gadolinite was found, partly imbedded in the bed-rock at the north-east corner of the hill, that measured thirty-six inches long,

* The development was undertaken under the auspices of the Nernst Lamp Company, of Pittsburgh, Pa., to whom all the output was sent.

eleven inches thick at the widest part, and weighed a little over two hundred pounds. It was apparently free from alteration, had specific gravity of 4.28 (taken on a very pure fragment), had a bright green chatoyancy at certain angles, and was like glass in its broad obsidian-like conchoidal fracture.

Upwards of a pound of very pure nivenite and not exceeding an ounce of mackintoshite, were picked out of the many boxes of mixed cyrtolite, fergusonite, and thoro-gummite. Only the density of nivenite saved it from being thrown away as magnetite (very abundant at this mine), and but for its associations it would be always neglected except by the expert mineralogist. Equally so with the mackintoshite, its resemblance to the dark cyrtolite and intimate association with it, prevents it from being recognised by the miner or layman. Some day this mine promises to be worked for the two last named minerals alone and as the main object of working there, and in the deeper working they should be found abundantly and in a higher state of purity.

Tengerite (?)—About ten grms, of a white mineral, occurring in semi-globular and flat radiated concretions in the cracks and fissures of the gadolinite, were finally obtained after much labour and search. This quantity was the result of detaching the mineral, bit by bit, from over 300 kilos. of fresh gadolinite. Since the composition of tengerite (to which species this substance is tentatively referred) is unknown, I submitted the rare mineral to Dr. W. F. Hillebrand, of the U.S. Geol. Survey, for analysis; his report is given in full below. The surprising feature is the presence of glucina (BeO) in the form of carbonate, which is new to science, and this may perhaps indicate a new glucinum mineral mechanically mixed with a basic hydrous carbonate of the rare earths of the yttrium group.

Dr. Hillebrand's Report and Analysis.

"The purest material that could be picked out, from that at my disposal, showed some brown admixture with the white. The following results were obtained from 0.3640 gm. of this selected material, after deducting 0.0262 gm. of residue, left after long treatment of the ignited powder with cold and quite dilute nitric acid.

Y ₂ O ₃ group	40.8	per cent	Mol. wt. ..	226
Ce ₂ O ₃ group	7.0	"	" ..	355
Fe ₂ O ₃	4.0	"	" ..	
BeO (Glo)	9.7	"	" ..	
CO ₂	19.6	"	" ..	
H ₂ O above 105° ..	14.1	"	" ..	
H ₂ O below 105° ..	3.2	"	" ..	
SiO ₂	0.4	"	" ..	
MgO, Alk., loss ..	1.2	"	" ..	

100.0

All determinations were made on the one portion, the CO₂ and H₂O being directly and simultaneously ascertained by ignition in a tube and collection of the escaping gases. The loss in weight of the ignited powder agreed with the sum of the CO₂ and H₂O found. Approximate molecular weight determinations of the earths, separated into two portions by potassium sulphate, gave 335 for the cerium group and 226 for the yttrium group, the last being the molecular weight of yttria itself. It is certain that some, if not all, of the ferric oxide reported is foreign to the carbonate, but how much it is impossible to say. The calculated ratios lead to nothing definite, except that the white mineral appears to be a hydrous basic carbonate, but whether a double carbonate of the rare earth metals and glucina, or a mixture, there are no present means of deciding."

Radio-activity.—All the minerals of Barringer Hill have been experimented with to ascertain the extent of this form of energy present. As early as September, 1902, the writer was at work upon it, and had then made successful radiographs from specimens mined at this locality as far back as 1889. In the order of their activity, as

shown by their own radiographs, I here mention the species in which the phenomena were observed.

Nivenite (which is a very soluble variety of uraninite) exhibited the most pronounced radio-activity, and beautiful radiographs were made by placing the mineral outside of a photograph plate-holder. Better ones were procured by placing the mineral in direct contact with the sensitive plate—"Cramer's X-ray." Twelve hours exposure, in the dark, developed very good interference figures; but with forty-eight hours, and up to five days exposure, the outlines became as sharp almost as are shown in photographs by sunlight.

Mackintoshite (which is the parent mineral of thoro-gummite) was next in the amount of radio-activity exhibited. It showed about half the intensity of nivenite when compared with equal exposures of the two minerals, side by side, on the same plate.

Positive evidence of the occurrence, within mackintoshite, of little crystals having even a *higher radio-activity* than that shown by the nivenite, was proven by developing the plates used with direct contact. Little-bright spots appeared in the field where the less energetic mackintoshite had touched it, and a dull grey border (made by the thoro-gummite coating) united to make a radiograph having *three* degrees of intensity from one mineral specimen. With a strong lens these bright spots, possibly due to a new species, could be identified upon the flattened surface, and they were noticed to be very unlike the surrounding mackintoshite. They resembled galena in colour and in metallic lustre, and were quite evenly distributed over the several flat sections examined. Mackintoshite has given evidence, in thin sections, of being translucent, and of a very dull green colour by transmitted light, but as the purest material yet analysed showed (*vide* Hillebrand's analysis) 4.31 H₂O present, it is possible that these little bright spots are only the normally pure anhydrous mineral. It is tenable also that these little inclusions, with their high radio-activity, are but a normally pure form of nivenite in which only UO₂ is present. Since mackintoshite can be rationally interpreted as being a mixture of three parts of thorite with one of uraninite (nivenite), the assumption that a new mineral has been discovered may not stand. The question is certainly one of unusual interest at this time and merits further investigation.

Thoro-gummite.—Contact radiographs of this mineral, made from a flattened surface after forty-eight hours exposure, in the dark, had much the appearance of ordinary sunlight photographs. All the minute details of structure and varying degrees of radio-activity were beautifully portrayed. It was surprising to note how perfect a picture this mineral could make of itself without any outside aid other than a photographic plate and a long exposure in the dark.

Masses up to a pound weight were found, and this proves that mackintoshite will not be as rare as it is now, when the mine is worked down to lower levels; for thoro-gummite is only an alteration product of mackintoshite, it having assumed one more molecule of water and changed its UO₂ to UO₃, and its colour from an apparent jet-black mineral, of specific gravity 5.50, to a dull yellow-brown mineral having specific gravity 4.54+. Long square prisms, like those of zircon, with simple terminal pyramidal planes, were observed.

Yttrialite.—This species gave better radiographs from its altered red crust and its yellow ochreous variety than from the pure dark grey-green anhydrous mineral. All of its radio-activity must emanate from the ten to twelve per cent of thorium present. Hillebrand's last analysis has shown that its composition can best be interpreted by assuming that it is a mixture of an yttrium silicate with the thorite molecule (both anhydrous). Slabs of this mineral eight inches long and six inches broad were broken from some of the larger masses, thus affording fine opportunity for large experimentation in testing it radio-graphically.

Fergusonite.—The mono-hydrated variety made the best

radiographs, but all the varieties (of which there are four at the locality) showed more or less action upon the sensitive film.

A new association was discovered in this species. Symmetrically compounded crystals of nivenite with fergusonite were found in the south walling of the hill. Long square prisms of nivenite with flat terminations had in their centres an equally long but tapering pyramidal crystal of fergusonite, in parallel position. Some of these were one inch long and one-quarter inch thick. The fergusonite was of the purest kind and almost transparent, and somewhat resembled the famous Spanish sphalerite.

Cytrolite.—Many hundred pounds were found and in great variety of form and colour. All kinds of it gave good radiographs after twenty-four hours exposure. Plates of it as large as one's hand, covered on one side with curved crystals, were not rare. It sometimes encrusted large quartz crystals to the depth of one inch, having radiate structure, and thus afforded a new feature for this mineral and one very uncharacteristic of zircon.

Radial Lines from the Ore Masses.—As early as December of 1902, my attention was attracted to the strange occurrence of unusually long radial lines projecting in many directions from the bodies of ore richest in thorium, uranium, and zirconium. I then named these occurrences "stars," and eagerly sought for them, as positive "pointers" to ore. At last I was obliged to give these "stars" more than passing attention, and here state the reason: While removing, piece by piece, a seventy-pound mass of mixed zirconium-yttrium-uranium and thorium ore, which was a nucleus to one of the best marked of these "stars" from its quartz matrix, my hands and face would begin to burn as if from the effect of strong sunlight, and after two or three days of this kind of mining a redness of skin and a burning sensation would be followed by actual soreness of the parts of my hands and face exposed to the direct emanations from the minerals. My assistant (Mr. J. Edward Turner) complained of it also, and asked me "if these minerals could be poisonous?" As no arsenic was present, the soreness which we both experienced might possibly have been caused by free fluorine, but not by any soluble constituent of the mineral, since salts, such as would be dissolved by the moist skin, had long ago been dissolved, leached out, and re-deposited in the "chimney" of the mine. It was some time after this that the thought came to me that this action might be the work of a radio-active element, and it is offered now more as a suggestion than as a proven fact. I incline strongly to the idea, however, of my having actually experienced the proof of the presence of a very high degree of radio-activity, of a peculiar if not unique kind, at this mine, and that the symptoms above described go a long way towards proving it. Of the true nature of this activity I will not at this time offer any conjectures, but will defer a discussion of it to a paper which is under preparation relating to this very interesting region.

Many photographic records were taken of these "stars;" they are sometimes eight or ten feet across. Although these radial lines are not new to science, having often been noted elsewhere in connection with allanite, monazite, and other rare species, it is not likely that they have been before observed on so large a scale. The cause of this phenomenon has not been determined, so far as I am informed, but it is not without interest that these radial lines are noted only with certain minerals containing rare elements, and are most conspicuous with the radio-active species.—*American Journal of Science*, xix., No. 114.

Microscopic Examination of Metals.—Messrs. R. and J. Beck, 68, Cornhill, have just issued a Catalogue of all the appliances and instruments for the preparation and examination of metals by means of the microscope. As many metallurgists have difficulty in obtaining supplies for this branch of work, our readers may be glad to know that such a catalogue exists and will be sent free on application.

THE USE OF COPPER IN DESTROYING TYPHOID ORGANISMS, AND THE EFFECTS OF COPPER ON MAN.*

By HENRY KRAEMER.

It is said that "the life of a Londoner is worth ten to fifteen years' less purchase than that of the average provincial. This fact is due to many causes, but the chief among them is the quality of the water." The same could be said of the residents of many of our American cities. Yet the necessity for a pure-water supply has been recognised since ancient times, and enormous sums of money have and are being spent in the control and purification of water supplies. Our failure to secure pure water has been largely due to ignorance on the one hand, in the past at least, and to mismanagement on the other. It was only in 1873 that Balfour Stewart wrote ("The Conservation of Energy," Chap. I., August, 1873):—

"It is only very recently that we have begun to suspect a large number of our diseases to be caused by organic germs. Now, assuming that we are right in this, it must nevertheless be confessed that our ignorance about these germs is most complete. It is perhaps doubtful whether we ever saw one of these organisms, while it is certain that we are in profound ignorance of their properties and habits. . . . We are at any rate intimately bound up with, and, so to speak, at the mercy of, a world of creatures, of which we know as little as of the inhabitants of the planet Mars.

"Yet, even here, with profound ignorance of the individual, we are not altogether unacquainted with some of the life habits of these powerful predatory communities. Thus we know that cholera is eminently a low level disease, and that during its ravages we ought to pay particular attention to the water we drink. This is a general law of cholera, which is of the more importance to us because we cannot study the habits of the individual organisms that cause the disease.

"Could we but see these, and experiment upon them, we should soon acquire a much more extensive knowledge of their habits, and perhaps find out the means of extirpating the disease, and of preventing its recurrence."

During the past thirty years, since Balfour Stewart wrote these lines, the whole subject of bacteriology has been developed and a distinct science has been created. In many industries bacteriologists are regularly employed to study the problems connected with them and to apply the results so obtained. In those industries which are in the hands of progressive private individuals and corporations, as of brewing, every scientific fact is considered on its merits and utilised if found applicable. On the other hand, the purification of water supplies being, for the most part, in the hands of municipalities, there are many factors which enter into the problem and which render progress very slow. In this connection, however, it is gratifying to note that sufficient progress has been made, in New York City, for instance, to show that the problem is no longer to be considered a political or partisan one. In February of this year the newspapers (*Public Ledger*, February 22, 1905) reported as follows:—

"The spectacle of Mayor McClellan and his old-time rival, ex-Mayor Seth Low, appealing to the State Senate at Albany to-day in favour of the passage of the Mayor's Bill to furnish New York City with a sufficiency of water, is a somewhat moving one. Mayor McClellan's argument in support of his own Bill, according to reports, was no wit less earnest than that of Mr. Low. The non-partisan character of the Mayor's proposal was further attested by the fact that the measure was supported by members of the Low administration."

The problem of the purification of water supplies in the United States, barring for the time being the pollution

* From the *American Journal of Pharmacy*, vol. lxxvii., No. 6.

caused by algæ, may be said to consist essentially of a study of typhoid organisms and of devising measures for their eradication.

The Distribution of Typhoid Organisms.

In the American edition of "Nothnagel's Encyclopedia of Practical Medicine," in the volume on typhoid fever and typhus fever, by Dr. H. Curschmann, edited with additions by William Osler, M.D., on page 38 it is stated:—

"Under the most varied ordinary conditions (not induced experimentally) the typhoid bacillus is capable of surviving for days, weeks, and months, and even for more than a year, and under favourable conditions even throughout the winter. An additional conclusion is permissible, namely that not alone the persistence of the germs, but also their dissemination through the media named, is certain. If in this connection the liquid media in general predominate, the dry media are not to be left out of consideration. It cannot be denied that the contagium attached to particles of dust may be disseminated through the air to a limited degree."

We have, therefore, the highest authority for believing that, contrary to the usual acceptance, the typhoid organism may persist for a considerable period of time, and that infection may occur in very many ways, as through drinking-water, food, and even through the air. In my own experiments I have found that at the ordinary temperature the typhoid bacillus will live over four months in both tap and distilled water, although the organism loses some of its characteristics after two months in that bouillon cultures will not give the agglutinating test with blood of a typhoid patient. (Paper read at the general meeting of the American Philosophical Society, April 13, 1905).

While the isolation of typhoid organisms from water is attended with considerable difficulty, still it has been supposed that when the water supplied a community is free from colon bacilli, it is likewise free from typhoid organisms; that is, the absence of colon bacilli is considered to mean the absence of sewage or fecal organisms. Some recent investigations would seem to indicate that *colon bacilli* are more widely distributed than formerly supposed, and that their presence in water may not always indicate fecal contamination (Erastus G. Smith, "Note on the Occurrence on Grain of Organisms resembling the *Bacillus coli communis*," *Science*, May 5, 1905, xii., No. 540, p. 710). However this may be, the absence of this organism must still be considered one of the best indications of an unpolluted water.

Next to water, milk is considered to be one of the most common sources of typhoid fever; but where the matter has been investigated it has been found that the milk was contaminated with water containing sewage organisms. Chapin, in his book on "Municipal Sanitation in the United States," page 511, cites an instance of this kind in the tracing of an epidemic of typhoid fever in Springfield, Mass., some years ago. He says:—

"The contents of the privy were spread on a lot near the well, and the men walked over this in going to the well, and their boots were rinsed off on the plank over the well and the water below. In this water *Bacillus coli* was found. The cans of milk were cooled in this well and it was found that the water leaked into the cans. Another chance for contamination was directly from the infected hands of convalescents."

Oysters and shell-fish taken from beds near where sewage is discharged have also been found to be a source of the disease.

Recently it has been shown by Dr. Benjamin Lee (Editorial comment in *Amer. Medicine*, November 26, 1904, p. 906), of the Pennsylvania State Board of Health, that water-cress may collect a sufficient amount of extraneous organic matter containing colon bacilli to be a source of infection.

While it is usually conceded that typhoid organisms are chiefly disseminated through water and milk, yet the free

use which is made of privy manure or night-soil in some localities as a fertiliser on truck farms renders it probable that fecal bacteria, including typhoid, are disseminated through the use of garden vegetables. In many instances this manure is allowed to stand in large pools, and by means of dippers is sprinkled over the soil. In August, during the heavy rains, I have seen low plants like lettuce and spinach completely washed with this more or less dilute liquid manure.

The experiments of Dr. Lee show how difficult it is to wash out the organisms from cress, and the same would apply to vegetables like lettuce and celery, in the latter case the soil being sometimes heaped up around the plants to prepare them for the market. No doubt in many instances certain fruits which are eaten in a raw condition, as tomatoes, apples, pears, &c., are sources of infection.

In a recent paper Dr. Barringer (*The Virginia Medical Semi-Monthly*, February 12, 1904, p. 501) gives a number of observations which tend to show that the dust from American railroad beds, through the discharge of typhoid patients while travelling over the roads when in the infective stage, is a probable source of typhoid infection, which has not been generally appreciated.

The Removal or Destruction of Typhoid Organisms in Food and Water.

Heretofore there have been two principal methods for the removal of typhoid organisms from drinking water, namely: (1) Filtration on a large scale, and (2) filtration and boiling on a small scale. Many bio-chemical methods for the purification of water have been proposed, some of which may be enumerated:—

1. Aqua regia followed by sodium carbonate.
2. Bleaching-powder followed by sodium bicarbonate.
3. Various permanganates, as potassium, calcium, aluminium, or barium.
4. Perchloric acid.
5. Bromine followed by ammonia.
6. Iron chloride and sodium carbonate.
7. Sodium bisulphate.
8. Peroxide of chlorine.
9. Kerosene.
10. Silver salts.
11. The alum process has been used for purifying the water supplies of large cities.

The use of electricity (12), as also of ozone (13) has been proposed.

The use of copper (14) for the purification of water on a large scale was first proposed by Dr. Moore and Mr. Kellerman, in a Bulletin of the U.S. Department of Agriculture a year ago. In a second Bulletin issued some weeks ago the authors have confirmed the efficiency of copper in the purification of water contaminated by algæ. They also report in one instance the abatement of an epidemic of typhoid fever in New Mexico, after treatment of the water-supply with copper sulphate. At Columbus, O., the water was treated with copper sulphate during September, October, November, and December, when the number of typhoid cases was reduced to from four to sixteen per month. The treatment was discontinued and the number of typhoid cases rose from 91 to 376 per month during January, February, and March.

That copper has a marked toxic or oligodynamic action on fecal bacteria, including typhoid bacilli, has been known since the experiments of Israel and Klingmann (*Virchow's Archiv*, 1897, cxlvii., pp. 293-340) were reported in 1897, and their observations have been confirmed by Moore and Kellerman and by every one who has worked along these lines since. (See papers by M. E. Pennington, N. Gildersleeve, and A. H. Stewart in *American Journal of Medical Sciences*, May, 1905; and by W. P. Mason, *Science*, April 28, 1905). I have found that when copper foil is allowed to remain in distilled water from one to five minutes sufficient copper is dissolved by the water to kill typhoid organisms within two hours.

The Effects of Copper on Lower Animals and Plants.

It is well known that the action of copper salts upon both plants and animals varies quite considerably. Seeds, for example, may be treated with quite concentrated solutions of copper sulphate without impairing their germinating activities. I have sprayed certain plants, as the common plantain and poison ivy, with ten per cent copper sulphate solutions without noticing any ill effects. Very many plants withstand spraying with solutions of copper sulphate containing as much as 1 part per 1000. The effects vary greatly according to the conditions which surround the plant. Seedlings of pea and corn, for instance, are killed when placed in solutions of copper sulphate 1 part to 200,000; but when the seedlings are placed in soil containing 1 part or even more of copper sulphate in 2000 parts of soil they remain uninjured.

Nägeli's experiments, performed during the '80's, showed that certain unicellular plants, as the algae, were killed by solutions containing exceedingly minute quantities of copper ("Ueber oligodynamische Erscheinungen in lebenden Zellen," *Neue Denkschriften der schweizerischen naturforschenden Gesellschaft*, xxxiii.-xxxiv., 1893-1895). His experiments have been repeatedly confirmed, and Israel and Klingmann observed a similar toxic action on other unicellular plants, notably some of the fecal bacteria and also on some of the unicellular animal organisms.

While there are these experiments showing that certain plants and animals are killed by solutions containing as little as one part of copper to 1,000,000,000 of water, still there are other plants which are stimulated and under certain conditions even appear to be benefitted by its presence. Frank and Kruger (*Ber. d. Deutsch. Bot. Ges.*, 1894, xii., p. 8) have shown that if potato plants are properly supplied with copper, the plants are hardier, yield a larger crop, and live longer than they otherwise would.

We may say in a general way that there are certain organisms which manifest a specific sensitiveness towards copper, including bacteria, one of the annelid worms, as well as other human parasites, while others are unaffected or even stimulated by relatively large quantities of copper sulphate. The unicellular organisms are the ones which appear to be most sensitive to the action of copper.

(To be continued).

BIBLIOGRAPHICAL NOTES ON TANTALUM AND THE OCCURRENCE OF TANTALUM IN FRANCE.

The following may be looked upon as the principal papers published on the application of tantalum to incandescent electric lamps.

M. Von Bolton, chemist to Messrs. Siemens and Halske, and M. Feuerlein, engineer to the same firm, have described their researches extending over several years, in a paper read before the Electrotechnischen Verein of Berlin, on January 17, 1905, and their communications were published by the *Electrotechnische Zeitschrift* of January 26.

M. Banville gave the Société Internationale des Electriciens at its meeting in May, a paper on incandescent lamps, in which he referred particularly to those of tantalum. Finally, M. Bolton has also published his researches in the *Zeitschrift für Elektrochemie* of January 20.

The success of the tantalum lamp should draw attention to the sources of this rare and precious metal. It is not met with frequently in France. According to the recent work of Schilling, the following are the deposits or minerals in which it is found; a few others ought to be added, such as that of Beauvoir, which has been acquired by Messrs. Siemens and Halske.

Tantalite.—Is met with at Chantelaube near Limoges. It contains 82.98 per cent of tantalum, with iron, tin, manganese, and silica, according to the analysis made by

M. Damour (*Comptes Rendus*, vol. xxv., p. 670). Other samples from the same locality contained 78.98 per cent of tantalum, with zirconium, tin, iron, and manganese, according to the analysis made by Jenzsch (*Poggendorfer Annalen*, vol. xcvi., p. 107); and 79.89 per cent of tantalum, with tin, manganese, iron, calcium, and copper, according to Chaudler and Rose (*Poggendorfer Annalen*, vol. civ., p. 100.)

Tungsten Ochre.—Is found at Meymac, in Correze; it contains from 1.1 to 5.0 per cent of tantalum, according to the analysis of Carnot (*Comptes Rendus*, vol. lxxix., p. 637).

Neotantalite.—Is found in the mines of zinc and kaolin at Colettes and Echassières in Allier; it contains from 22 to 23.1 per cent of niobium, and from 57.7 to 60.58 per cent of tantalum, with iron, manganese, tin, potassium, sodium, lithium, silicon, aluminium, calcium, magnesium, and uranium, according to the analysis of Pisani and Ternier (*Zeits. für Krist. Min.*, vol. xxxix., p. 183; *Bull. Soc. Trans.*, vol. xxv., pp. 34-38).—*Bull. Soc. d'Encouragement pour l'Industrie Nationale*, June 30, 1905, p. 800.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 26, June 26, 1905.

Hydrolysis of very Concentrated Solutions of Ferric Sulphate.—A. Recoura.—The author finds that a very concentrated solution of ferric sulphate in a well-corked flask spontaneously decomposes into a solid basic sulphate of well defined composition, $6[\text{Fe}_2\text{O}_3, 3\text{SO}_3] \cdot \text{Fe}_2\text{O}_3 \cdot \text{Aq}$, which is only slightly soluble and of a yellowish white colour, and also a soluble acid sulphate or a mixture of neutral sulphate and free acid. This decomposition is not instantaneous; it is a function of the time. The rapidity and amount of the decomposition are greatly influenced by different circumstances which the author investigates.

Compounds of Aluminium Chloride and Carbon Oxychloride.—E. Baud.—When carbon oxychloride is liquefied over anhydrous aluminium chloride, this salt entirely dissolves, and if it is then left to itself at ordinary temperatures for the excess of gas to be evolved, a colourless liquid product remains, which solidifies at -2° , and has for its composition (1) $\text{Al}_2\text{Cl}_6, 5\text{COCl}_2$. The author also proves the existence of the two further compounds, (2) $\text{Al}_2\text{Cl}_6, 3\text{COCl}_2$, (3) $2\text{Al}_2\text{Cl}_6, \text{COCl}_2$. The compound (2) corresponds to the neutral carbonate, $\text{Al}_2\text{O}_3, 3\text{CO}_2$, which has not hitherto been isolated. The last compound is present in commercial aluminium chloride. Finally, the solution of aluminium chloride in liquid carbon oxychloride will probably be able to effect syntheses which were not possible with solid aluminium chloride.

Constitution and Properties of Tin Steels, Titanium Steels, and Cobalt Steels.—Léon Guillet.—The author's researches on tin, titanium, and cobalt steels show that these metals enter into solution with the iron, and that the carbon of these steels is, at least within the author's experimental limits, in a state of iron carbide. The mechanical properties of these steels show them to be of practically no commercial importance, but prove clearly the very sharp difference existing between tin, titanium, and silicon steels, on the one hand, and nickel and cobalt steels on the other.

Hydrogenation of the Aldoximes.—A. Mailhe.—The hydrogenation of the oximes can be easily effected by MM. Sabatier and Senderens' method of using finely divided nickel and hydrogen. Operating at a temperature between 180° and 220° the first product obtained is a

primary amine containing the same amount of carbon as the oxime, and produced according to the reaction $RC=NOH.R' + 2H_2 + H_2O + RCH.NH_3.R'$. At the temperature of the reaction, however, the nickel decomposes the primary amine according to the equation:—
 $2R' > CH.NH_2 = NH_3 + \left(\frac{R}{R'} > CH \right)_2NH$.

Bromuration of Paraldehyde.—P. Freundler.—The bromuration of paraldehyde at a low temperature causes the production of bromacetic aldehyde. This becomes crotonised above 0° in presence of hydrobromic acid, but the crotonisation is limited. In presence of an excess of bromine the dibromocrotonic aldehyde is transformed into tetrabromobutyric aldehyde, an inert and very stable substance, but whose chain is broken when placed in contact with hydrobromic acid. The complex $CH_2Br.CBr = CBr.CHO$ being very unstable.

Some New β -Ketoaldehydes.—F. Couturier and G. Vignon.—The authors prepare a number of new β -ketoaldehydes by Claisen's method modified by the use of metallic sodium on a mixture of formic ether and the particular ketone. The sodium salt of the ketoaldehyde formed when dissolved in ice-water, acidulated by acetic acid, and treated with copper acetate carefully freed from basic acetate, gives the copper salt of the ketoaldehyde, which can be purified by washing with petrol ether and crystallisations from ether. By this method the following compounds were prepared:—Diethylacetylaldehyde, $C_2H_5 > CH-CO-CH=CHOH$; trimethylacetylaldehyde, $C_2H_5 > CH-CO-CH=CHOH$; isovalerylaldehyde, $(CH_3)_3C-CO-CH=CH.OH$; isobutyrylaldehyde, $CH_3 > CH-CH_2-CO-CH=CHOH$; isobutyrylaldehyde, $\frac{CH_3}{CH_3} > CH-CH_2-CH_2-CO-CH=CHOH$.

Monomethylamine Iodomercurates and Chloriododomercurate.—Maurice François.—The author prepares monomethylamine iodomercurates and monomethylamine chloriododomercurate from monomethylamine by the action of mercuric iodide.

Derivatives of Butyrolin and Capronin.—L. Bouveault and René Locquin.—The authors investigate the properties and prepare a number of derivatives of butyrolin and capronin.

A Bivalent Phytosterine-alcohol.—T. Klobb.

The Combustion of Sulphur in the Calorimetric Bomb.—H. Giran.—The heat of formation of sulphurous anhydride from its elements in M. Berthelot's calorimetric bomb apparently increases with the pressure. The author supposes this increase to be due to the formation of persulphuric anhydride, which should increase with the pressure. To prove this hypothesis, he measures the heat of formation of S_2O_7 from SO_3 and O .

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 6, 1905.

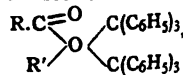
Complex Compounds of Pentavalent Vanadium with Tetravalent Elements.—Wilhelm Prandtl.—By warming a solution of selenious acid with vanadium pentoxide, yellowish red crystals (double refracting) are obtained, which are difficultly soluble in water. Their composition corresponds to the formula I. $3V_2O_5.4SeO_2.4H_2O + 6aq.$ or II. $3V_2O_5.4SeO_2.4H_2O + 10aq.$, the former being obtained from solutions containing excess of selenious acid, or on evaporating the vanadium selenious acid with hydrochloric acid, while the latter is prepared from exactly equal parts by weight of vanadium pentoxide and selenium dioxide. On dissolving the vanadium selenious acid in alkalis, alkali vanadium selenites are obtained, and of these two series may be prepared, the salts being red or yellow according to the proportions of V_2O_5 and SeO_2 used in their preparation. Neither series has the same type of formula as the free acid. The salts are prepared

by boiling definite quantities of vanadium pentoxide and selenium dioxide with water for a few minutes, adding the hydroxide and water till a clear, colourless, feebly alkaline solution is obtained. This is then acidulated with acetic acid, filtered, and allowed to crystallise. The salts which have been prepared thus are (red) ammonium vanadium selenite, (red) potassium vanadium selenite, (yellow) ammonium vanadium selenite from solutions containing excess of selenium dioxide, and yellow potassium vanadium selenite. The sodium and lithium salts being very readily soluble have not yet been prepared pure.

Action of Silent Electric Discharge upon Chlorine.—Franz Russ.—Using a high tension current obtained from the secondary coil of a large inductor provided with a Wehnelt interrupter, the author found that chlorine, when exposed to a silent electric discharge, suffers a decided change. The action of chlorine thus treated upon benzene was investigated, and it was found that:—1. By the simultaneous action of a silent electric discharge and light upon chlorine, active chlorine is prepared. 2. By the action of either light alone or the electric discharge alone only a very slight degree of activity is produced. A far greater quantity of active chlorine is obtained by the simultaneous action of these two factors. 3. The degree of activity depends upon the magnitude of the dielectric and upon the dryness of the chlorine. If the gas is led through water before being allowed to act upon the benzene it loses almost all its activity. 4. The chlorine retains its activity at ordinary temperatures even when led through tubes of considerable length, e.g., 200 c.m. Three experiments showed that the amount of benzyl chloride formed was the same as when the benzene was immediately behind the discharge vessel. 5. The activity is lost when the gas is heated. 6. The question whether the joint action of light and a silent electric discharge produces a new modification of chlorine analogous to ozone, or whether the activity is due to the formation of intermediate products, has not yet been decided. 7. When quartz vessels are substituted for glass, five and a-half to six and a-half times as much benzyl chloride is formed as in glass vessels under similar conditions. This is to be explained by the fact that quartz is far more transparent to ultra-violet rays than glass, and evidently most of the effect of daylight upon a mixture of chlorine and benzene is due to the ultra-violet part of the spectrum. The use of a quartz mercury lamp for illumination has the same effect.

Triphenylmethyl.—M. Gomberg and L. H. Cone.—Triphenylmethyl forms molecular compounds with esters, a large number of these compounds having been prepared and investigated. Their composition seems to be ex-

pressed probably by the formula



and thus one of the oxygen atoms has become tetravalent. Triphenylmethyl also forms compounds with the aromatic and unsaturated aliphatic hydrocarbons, and with a constituent of petroleum ether. All these addition products exhibit the characteristic reactions of triphenylmethyl, forming the peroxide, $(C_6H_5)_3C.O.O.C(C_6H_5)_3$, on addition of oxygen.

Mercuric Fulminate.—Lothar Wöhler and K. Theodorovits.—When nitric acid containing no oxides of nitrogen is employed in the preparation of mercury fulminate by the usual method the reaction is only very feeble, and small quantities of metallic mercury are formed. The same holds good when lignone is substituted for alcohol. Acetaldehyde acts upon an ice-cold solution of mercury in concentrated nitric acid, the reaction taking place instantaneously and white fulminate being formed. Dimethyl acetal also acts in the same way, but not so vigorously. As aldehyde is an oxidation product of alcohol it was to be expected that the process would be simpler with acetal than with alcohol, and simplest with aldehyde, and this was found to be the case. The action with alcohol is by far the least energetic, and the product

is always coloured grey or yellowish brown, owing to the presence of metallic mercury. Methyl alcohol gives no fulminate, nor do propyl alcohol, aldehyde, acetone, and methyl ketone in the ordinary way. Thus it appears that a di-carbon chain is necessary for the formation of the fulminate, and that no fulminate is formed unless the methyl group is present in the alcohol, acetals, aldehyde, and its polymers. The CH_3 group, moreover, must be combined with CH_2OH , or $\text{CH} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$, or $\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$, or $\text{C} \begin{smallmatrix} \text{H} \\ \diagdown \text{O} \end{smallmatrix}$; CH_3CN , for example, only reacts feebly, and no fulminate is formed.

Palladium.—C. Paal and Conrad Amberger.—The authors find that the reduction of palladium salts by means of hydrazine sulphate, both in acid and alkaline solution, leads to the formation of elementary palladium. They explain this contradiction of Jannasch and Bettges' results by supposing that these authors had either confused their preparations with the oxygenated preparations which had been ignited in air, or else that the hydrogen used for the reduction acted in presence of the oxygen of the air, when finely divided palladium would act catalytically (like platinum), forming water, even in the cold. When performing these experiments the authors always expelled the air by means of carbon dioxide before allowing hydrogen to act upon their preparations.

Solid Solutions of Indifferent Gases in Uranium Oxides.—V. Kohlschütter and K. Vogdt.—The authors studied the compound of uranic acid and hydroxylamine with a view to discovering in what condition helium is present in uranium minerals. They found that on heating uranic acid hydroxylamine to 125° a slow intramolecular decomposition of the hydroxylamine takes place, N_2 , N_2O , NH_3 , and H_2O being formed. The ammonia and water escape, but the nitrogen and nitrous oxide remain practically quantitatively dissolved in the uranic acid. Apparently they form a perfectly homogeneous mixture with it, from which they escape when the substance is dissolved in acids. On heating *in vacuo* the preparation still retains the gases up to about 300° , and apparently the uranium oxide only possesses the power of dissolving the indifferent gases as long as it contains a definite amount of water. From experiments with cleveite the authors are persuaded that only minerals with a certain amount of water in them contain any appreciable quantity of helium.

MISCELLANEOUS.

British Pharmaceutical Conference.—The forty-second annual meeting of this body was opened at the Hotel Metropole, Brighton, on Tuesday, July 25th. This is an organisation distinct from the Pharmaceutical Society, and is solely concerned in "the encouragement of pharmaceutical research, and the promotion of friendly intercourse and union amongst pharmacists," whereas the Pharmaceutical Society is a statutory body charged with the administration of the Pharmacy Acts, and the examination and registration of those who desire to be registered under these Acts. The Conference was received by the Mayor and Mayoress at the Royal Pavilion on Monday evening, and on Tuesday morning the President, Mr. W. A. H. Naylor, F.I.C., F.C.S., of London, delivered an address. Thereafter satisfactory reports of the position of the Conference were submitted, and the reading and discussion of communications resulting from researches was commenced. It was attended by nearly 300 pharmacists from all parts of the United Kingdom, and several Colonial chemists are amongst the number.

International Congress for the Study of Radiology and Ionisation, Liège, 1905.—The first International Congress for the Study of Radiology and Ionisation will be held during the present year at Liège, between the 12th

and 14th of September (inclusive). The Congress will be divided into two sections:—**Physical Section.**—I. The Physics of Electrons, including radiations of various kinds. II. Radio-activity and Dependent Transformations: The activity of waters and earths; Radio-active deposits. (The above outlines of the work to be considered as suggestive rather than limiting. The programme is intended in fact to include the study of all questions having to do with radio-activity). III. Meteorological and Astronomical Phenomena and their relation to ionisation and radio-activity. **Biological Section.**—The programme governing the work of this section will include an examination of the physiological properties of various radiations and of radio-activity, and will consider their medical value and application. The method of procedure in this section will be determined upon by a special commission presided over by Professors Bouchard and d'Arsonval, members of the Institut de France, and of the Academy of Medicine of Paris. Beside this special commission, a general committee, composed of men notable for research work in matters of interest to this investigation, and presided over by M. Henri Becquerel, will examine, classify, and approve such reports, papers, and notes as may be offered. Intending contributors are requested to forward the manuscript of their papers at their earliest convenience, and the titles immediately if possible.

The Evolution of Oxygen observed during the Decomposition of Cupric Metaborate.—W. Guertler.—On evaporating a solution containing one molecule of nitrate of copper and 2 molecules of boric acid, and heating the residue without exceeding a temperature of 950° , we obtain blue crystals of the metaborate $\text{B}_2\text{O}_4\text{Cu}$. These crystals are doubly refracting, $D=3.859$; they are unattacked by dilute mineral acids, and have the hardness of corundum. When fused they form a black glass more easily attacked than the crystals, having a density of 3.61 . The same metaborate is obtained more easily by the fusion of the nitrate with an excess of acid. After fusion we obtain two layers, the upper one of which forms a greenish glass soluble in water, and the lower one consists of blue crystals of the metaborate. If we raise the temperature to about 1000° , we obtain an abundant evolution of oxygen. Even at a lower temperature, by sufficiently prolonging the heating, we observe the formation of a red amorphous mass. The metaborate fuses at about 970° ; this constant, however, is difficult to determine, as the evolution of oxygen commences at about 875° . The loss of oxygen is about 5.3 per cent, and results from the decomposition of the metaborate according to the equation:— $6\text{B}_2\text{O}_4\text{Cu} = 3\text{Cu}_2\text{O} \cdot 2\text{B}_2\text{O}_3 + 3\text{O} + 4\text{B}_2\text{O}_3$. The new borate thus formed, $3\text{Cu}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, can be easily isolated by taking up the product of decomposition with water. It occurs as brown crystals having a greenish colouration on the surface. The author has not been able to reproduce this substance by the direct action of boric acid on protoxide of copper. —*Zeit. Anorg. Chem.*, vol. xxxviii., p. 456.

ST. PAUL'S SCHOOL, West Kensington. —

An EXAMINATION will be held at the above School on Tuesday, September 5th, 1904, and on the following days, for filling up about Twenty Vacancies on the Foundation. —Full particulars of the Examination can be obtained on application to the Bursar.

TO BE SOLD, the English Patent referring to Apparatuses for Wood Impregnation (mining) applicable to Tar Distillation and Founding, &c. Thirty-six installations have been started in Germany, with large profits. —For particulars address, in German, "K.D. 3573," Rudolf Mosse, Cologne.

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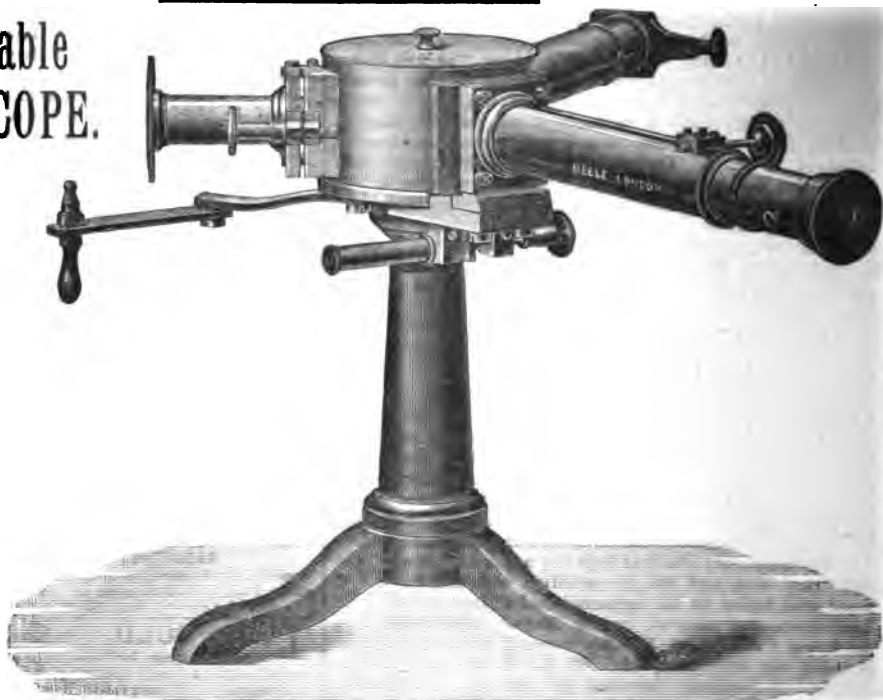
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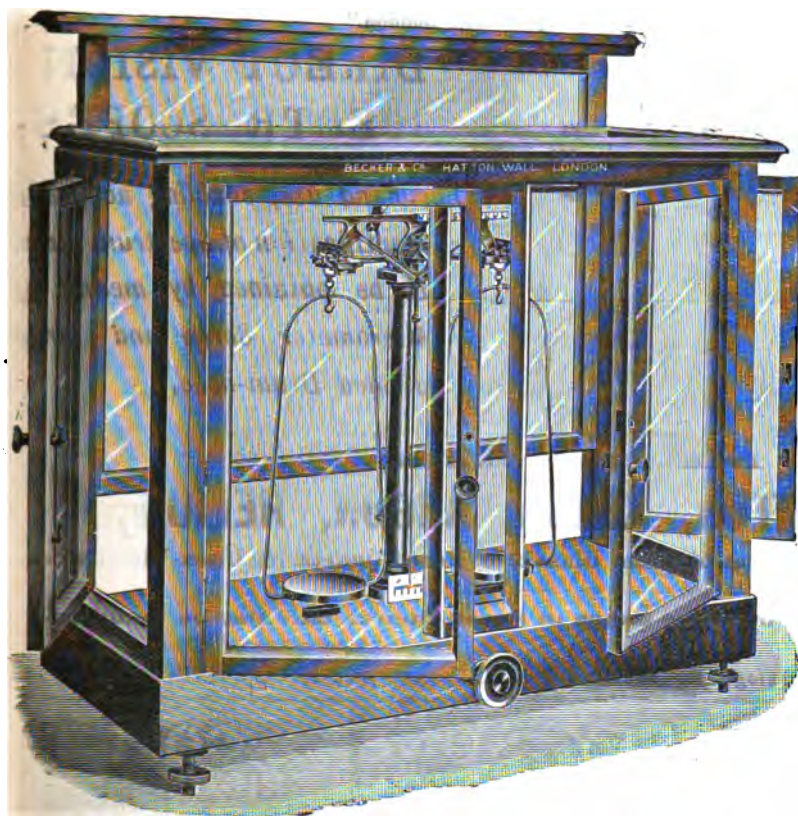
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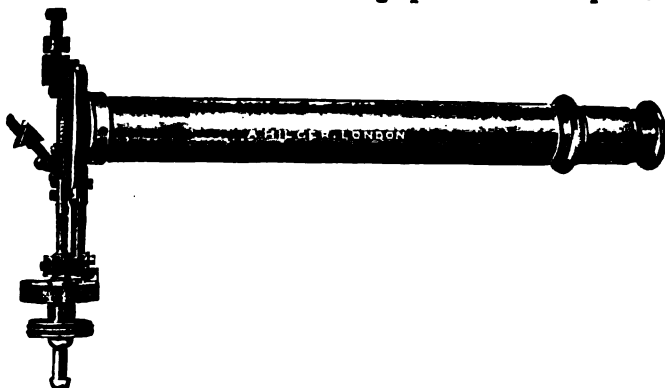
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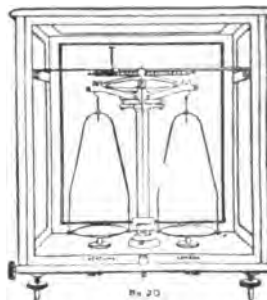
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THE CHEMICAL NEWS.

VOL. XCII., No. 2384.

THE PERCOLATION OF RAIN-WATER THROUGH SOILS.

By W. F. SUTHERST, Ph.D., F.I.C.

THE continued drought in the North and Midlands has naturally dried up the soil to a considerable extent; so much, indeed, that certain light soils are practically sun-dried to the depth of several inches, leaving the roots of the various crops growing in them more or less out of reach of any moisture. To see how much rain it actually needed to moisten the dried soil up to certain depths, a series of experiments was carried out here on various classes of soils.

A tube $1\frac{1}{2}$ inches in diameter was taken and filled with sun-dried specimens of soils and pressed down so as to resemble as near as possible their condition in nature. On these were placed from time to time portions of water equivalent to 0.1 inch and multiples of the same (2.5 c.c.). From this were noted—(1) The depth to which the water extended; (2) the time to reach this depth; and (3) the time the water remained on the surface of the soil before finally disappearing. The following tables give the figures obtained by these experiments:—

I.—Sandy Loam.

Inches of rain.	Depth. Inches.	Time.		Time on surface.	
		Mins.	Secs.	Mins.	Secs.
0.1	$\frac{1}{2}$	0	15	0	0
0.2	$1\frac{1}{2}$	0	40	0	1
0.3	$1\frac{1}{2}$	0	40	0	1
0.4	$1\frac{1}{2}$	0	45	0	2
0.5	$1\frac{1}{2}$	0	50	0	2
0.6	$2\frac{1}{2}$	1	0	0	$2\frac{1}{2}$
0.7	$2\frac{1}{2}$	1	15	0	$2\frac{1}{2}$
0.8	$2\frac{1}{2}$	1	20	0	$2\frac{1}{2}$
0.9	$3\frac{1}{2}$	1	30	0	3
1.0	$3\frac{1}{2}$	1	35	0	3

II.—Loam.

0.1	$\frac{3}{4}$	0	20	0	2
0.2	$1\frac{1}{2}$	0	50	0	6
0.3	$1\frac{1}{2}$	1	30	0	12
0.4	$1\frac{1}{2}$	2	0	0	23
0.5	$1\frac{1}{2}$	3	0	0	35
0.6	$2\frac{1}{2}$	4	0	1	0
0.7	$2\frac{1}{2}$	5	15	1	30
0.8	$2\frac{1}{2}$	6	35	2	50
0.9	$3\frac{1}{2}$	7	50	4	0
1.0	$3\frac{1}{2}$	9	20	5	20

III.—Clay Loam.

0.1	$\frac{1}{2}$	0	50	0	20
0.2	$\frac{1}{2}$	2	30	1	15
0.3	$\frac{1}{2}$	4	0	2	0
0.4	$1\frac{1}{2}$	6	15	2	30
0.5	$1\frac{1}{2}$	8	0	3	0
0.6	$1\frac{1}{2}$	10	15	4	0
0.7	$2\frac{1}{2}$	14	10	4	45
0.8	$2\frac{1}{2}$	20	30	5	20
0.9	$2\frac{1}{2}$	27	15	6	35
1.0	$2\frac{1}{2}$	35	10	8	0

IV.—Heavy Clay Soil.

		Hours.	Mins.		
0.1	$\frac{1}{2}$	0	4	2	30
0.2	$\frac{1}{2}$	1	0	20	0
0.3	$\frac{1}{2}$	2	50	45	0
0.4	$1\frac{1}{2}$	4	0	60	0
0.5	$1\frac{1}{2}$	7	0	90	0

V.—Garden Soil.

		Mins.	Secs.		
0.1	$\frac{1}{2}$	0	40	0	5
0.2	$\frac{1}{2}$	0	50	0	8
0.3	$1\frac{1}{2}$	1	5	0	10
0.4	$1\frac{1}{2}$	1	20	0	15
0.5	$1\frac{1}{2}$	1	40	0	19
0.6	$1\frac{1}{2}$	1	55	0	23
0.7	$2\frac{1}{2}$	2	20	0	28
0.8	$2\frac{1}{2}$	2	50	0	33
0.9	$2\frac{1}{2}$	3	20	0	40
1.0	$2\frac{1}{2}$	3	55	0	46

Experiments carried out some years ago by Lawes and Gilbert demonstrated that over 50 per cent of the rainfall is evaporated before it has the chance of percolating through the soil, so that really it would need more than twice the rainfall to penetrate the depths obtained by the above trials. As, however, the rain remains for such a long period on clay soils before percolating, it stands to reason that in these cases much more than 50 per cent of it must disappear by evaporation and draining from the surface, the latter more so in case of sloping lands.

The Agricultural College, Tamworth.

THE DECAY CONSTANT OF THE EMANATIONS OF EMANIUM AND ACTINIUM.

By O. HAHN and O. SACKUR.

THE decay constant of the emanation of Giesel's emanium has not yet been determined; its numerical value is of special interest in reference to the question whether emanium, as has often been suggested, is identical with Debierne's actinium. According to Giesel's qualitative statements, emanium emanation loses its activity after a few seconds.

We used for our measurements a preparation kindly placed at our disposal by Giesel. This was wrapped in paper, and placed in the front part of a glass tube filled with wadding; air was then blown over it into the measuring tube. The experimental arrangement was exactly similar to that employed in the experiments with radium emanation carried out by one of us (*Berichte*, 1905, xxxviii., 1753). A few seconds after the emanation had been blown in, the earth connection of the pair of quadrants connected with the measuring tube was removed. The electrometer needle was deflected, but its rapidity became visibly less. After about half a minute the rapidity, and thus the conductivity, in the tube had become constant. In order to be able to establish the time this decrease of rapidity takes, we marked by pencil strokes the position of the image of the needle upon the scale after equal periods of time marked by the beats of a metronome (e.g., 1.3 sec.).

The calculation of the duration of life of the emanation from these measurements may be performed as follows:—The experiment gives us the distance of the needle from the zero-point as a function of the time. As special experiments showed, with the electrometer used the deflection of the needle is proportional to its potential v . Hence, we at once obtained its increase with the time, i.e., the function $v = f(t)$.

The increase of the potential dv in time dt is caused by the electricity passing through the interior of the measuring tube. This is proportional to the conductivity, and thus to the activity, of the emanation and to the induced activity produced on the walls. If we denote the former by i_1 and the latter by i_2 , then $\frac{dv}{dt} = i_1 + i_2$. According

to the known exponential law, $i_1 = i_0 e^{-\lambda t}$.

i_2 also decreases according to an exponential law, but so slowly that it may be regarded as constant during the few seconds the measurement takes.

Therefore $\frac{dv}{dt} = i_0 e^{-\lambda t} + i_2$, and, after integration,—

$$v = i_0 \int e^{-\lambda t} dt + i_2 t = -\frac{i_0}{\lambda} e^{-\lambda t} + i_2 t + C.$$

If $t=0$, $v=0$, and $C = -\frac{i_0}{\lambda}$; hence $v = \frac{i_0}{\lambda}(1 - e^{-\lambda t}) + i_2 t$.

After less than half a minute, as mentioned above, the rapidity of the deflection of the needle is constant, and thus is only determined by the magnitude i_2 , the induced activity; thus, i_2 is given by the experiment. Hence the value of $i_2 t$ can be calculated for each period of time, and can be deduced from the measured deflection v . In this way we obtain a corrected function, $v' = \frac{i_0}{\lambda}(1 - e^{-\lambda t})$,

which expresses only the increase of potential caused by the activity of the emanation itself. This equation is transcendental as regards the decay constant λ , and cannot be solved for λ . But the following consideration leads to its calculation.

After a sufficiently long time (less than half a minute), as experience shows, v' becomes constant, and the needle would remain still if it were not driven forward with the rapidity corresponding to the induced activity. This maximum value of v' is $v'(\text{max.}) = \frac{i_0}{\lambda}$. It has been directly

determined experimentally on many occasions, and on others, in which it would lie outside the scale employed, it can be determined accurately enough graphically by extrapolation.

Moreover, $\frac{v'}{v'(\text{max.})} = 1 - e^{-\lambda t}$, and therefore—

$$\lambda = \frac{1}{t} \log_e \frac{v'(\text{max.}) - v'}{v'(\text{max.})}.$$

The following method of calculation is simpler:—The value $\frac{v'}{v'(\text{max.})}$ is equal to $\frac{1}{2}$ if $e^{-\lambda t} = \frac{1}{2}$, i.e., in that time in which the activity of the emanation has sunk to half its value. Thus we obtain the so-called "half-period of life" as that period of time after which the deflection of the needle has reached half its maximum value, and this can be interpolated with great accuracy from the curves obtained empirically. The following example makes this method of calculation clearer:—

Time. Secs.	v . Scale divisions.
1.2	60
2.4	115
3.6	160
4.8	200
6.0	230
7.2	258
8.4	277
9.6	293
10.8	311
12.0	325

The constant residual activity amounted to 6 scale divisions in 1.2 seconds. Thus the following values are calculated:—

v' corr.	v' corr.
54	222
103	235
142	245
176	257
200	265

Extrapolation gives $v'(\text{max.}) = 290$. The half value 145 is reached after 3.7 seconds. After this time, therefore, the activity of the emanation has sunk to half its value. Three other series of experiments with the same preparation

gave the values 3.8, 3.3, and 3.3 secs., and three series with another preparation, which Giesel called emanium X, gave the values 3.6, 3.6, and 3.3 secs. The mean of all seven series is 3.6 secs. The absolute value of the decay constant λ is therefore $\frac{\log_e 2}{3.6} = 0.19$.

Exactly the same measurements were carried out with an actinium preparation kindly given us by Debiere. For the time in which the intensity of the emanation sinks to half its value we obtained the numbers 3.8, 3.9, and 4.0 secs. Thus the mean value was 3.9 secs., and the decay constant λ therefore equals 0.21. This agrees perfectly with the number given by Debiere, and the difference between it and the number obtained for emanium lies within the limits of experimental errors.

Contradictory statements are to be found concerning the time of decay of the induced activity resulting from emanium and actinium emanations. Debiere gives for actinium about 40 mins. (*Comptes Rendus*, 1904, cxxxviii., 411), and Miss Brooks the same for emanium (*Phil. Mag.*, 1904, [6], viii., 373). Giesel, on the other hand, from the measurements of Elater and Geitel, gives 34.4 mins. (*Berichte*, 1904, xxxvii., 3963), and Bronson 36 mins. (*Amer. Journ. Sci.*, 1905, [4], xix., 185). Hence we considered a new determination desirable.

We found the following method applicable for the production of a strong induced activity:—The emanation was led for several hours through a glass spiral, which was cooled by liquid air. The emanation condensed in this, and was transformed into induced activity. After stopping the current of gas the tube was washed out with warm hydrochloric acid, and the latter was evaporated to dryness in a little dish. The decrease of activity can be followed by measuring the rapidity of discharge of an electroscope. By this method we obtained for the induced activity produced by Debiere's actinium the following times of decay to the half value:—36.0, 36.2, 36.2, 37.0, 37.2 mins., the mean value being 36.5 mins., and the corresponding values for Giesel's emanium were 36.3, 36.3, 36.5 mins.; but it must be confessed that single series of experiments with both preparations led to somewhat higher values up to 40 mins. for some unexplained reason.

In any case it has been proved by our measurements that Debiere's actinium and Giesel's emanium produce the same emanation and the same induced activity. They are thus probably to be regarded as identical.

We are greatly indebted to Giesel and Debiere for sending their preparations, and to Sir William Ramsay for the trouble he has taken.—*Berichte*, 1905, xxxviii., 1943.

TANTALUM AND ITS ALLOYS.

MUCH interest has recently been shown by engineers, metallurgists, and others in the new uses to which the metal tantalum has been applied, particularly in the alloys of tantalum with steel. Messrs. Siemens, Halske, and Co., of Askaniischer Platz, Berlin, have just had granted to them a British patent for tantalum alloys, which are more particularly for use for bearings, cams, eccentrics, rollers, and those portions of machinery subject to great wear. They claim that their tantalum alloys with carbon and steel can be made almost as hard as a diamond.

The following information is extracted from Messrs. Siemens, Halske, and Co.'s specification:—

Tantalum possesses, like steel, the property of being easily worked and hardened; it has also great resistance to fracture and great elasticity. Its hardness can be increased to such an extent as to greatly exceed that of the best kinds of steel and that of the stones usually employed. As regards the greatest degree of hardness which it can attain, it is almost equal to the diamond. It has the further advantage over steel in being one of the precious

metals which is not affected by the atmosphere, and which, at ordinary temperatures, completely resists the action of most acids. In the case of mechanisms of precision this property is of the greatest importance. In order to be able to work the metal satisfactorily, it must be previously well fused. By the fusing process it is at the same time freed from impurities and brought to a state of a homogeneous body. The fusing is effected best *in vacuo*, and by means of the electric current.

The metal which has been melted can be readily worked mechanically in any known manner; it can be hammered, rolled, drawn, filed, and the like, and can thereby be wrought into every desired form. When being mechanically worked, the metal, in particular when it contains a small quantity of carbon or other hardening medium, readily assumes so great a degree of hardness that the further working is rendered impossible, and it must then be carefully re-heated or annealed in order to be again rendered soft. In this annealing process care must be taken that the temperature does not rise too high, as otherwise the material is more easily attacked by the oxygen of the atmosphere. The metal will, however, even in the form of the finest drawn wires or thinnest rolled bands, stand a heating in the open air, up to a dark red heat, without being appreciably affected. When so heated the metal shows a colouration similar to tempered steel. In order to prevent too great a heating, in particular of minute parts of metallic tantalum, it is preferable to effect the heating indirectly by raising large plates or drums to the temperature to which the parts to be heated are required to be brought, and then to bring the objects made of tantalum to be heated in contact with these plates or drums. If, on the other hand, it is desired to raise the objects made of tantalum to higher temperatures, without being materially affected on their surface, it is of advantage to effect the heating *in vacuo*, as at very high temperatures metallic tantalum combines with almost all known substances. The heating *in vacuo* is preferably effected by electrical means, such as by the use of electrical resistances or directly by passing an electric current through the objects to be heated. For imparting great hardness to the metallic tantalum other substances can be added thereto; in particular carbon serves for this purpose, which acts upon metallic tantalum in the same way as it does upon steel. But numerous other substances, such as oxygen, hydrogen, silicon, boron, aluminium, titanium, and tin can be used. When using carbon as the hardening medium the tantalum becomes very hard and resisting, even with the presence of a small fractional part of 1 per cent. Also, of the other above-named substances, only very small quantities are required in order to produce great hardness. If the mixture of such hardening substances is increased materially above the small proportions mentioned, the metallic tantalum generally becomes so brittle that no further working of the same is possible. The extent of the permissible quantity of carbon or other substances must be determined in each separate case according to the particular conditions and character of the substances chosen.

A subsequent hardening of already worked parts of soft metal can also be effected by heating the metal to redness in carbon, in a similar manner to the treatment of steel.

As metallic tantalum is at present very expensive, only those parts will, of course, be made of tantalum that are directly subject to strong mechanical action, such as the linings of bearings, the cones and balls for the ball bearings of machines and mechanisms, and the like. For many purposes also in place of pure metallic tantalum, alloys of the same can be used which exhibit good properties—for example, alloys of tantalum with iron. The most serviceable alloys of iron are, on the one hand, those which consist of iron containing only small quantities, up to a few parts per cent of tantalum, or which consist of tantalum having only a few parts per cent of iron. The properties of these alloys can be varied to a very great extent by varying the proportions of the constituents.—*The Times Engineering Supplement*, July 26, 1905.

NOTES ON HEAT INSULATION, PARTICULARLY WITH REGARD TO MATERIALS USED IN FURNACE CONSTRUCTION.*

By R. S. HUTTON and J. R. BEARD.

Introduction.

THE importance of a knowledge of the heat conductivity of the materials used for the bricks or linings of furnaces scarcely needs to be emphasised. There is no doubt that a careful study of this subject would enable a very large saving to be effected in the fuel or other heating costs in many experimental and industrial furnaces.

The manufacturer and purchaser of refractory products both seem to ignore the necessity for accurately determining the quality of their material so far as its heat insulating power is concerned. Their specifications are confined to other properties, but it is doubtful if any of them are of greater economic importance than the heat conductivity.

So far as laboratory crucible and muffle furnaces are concerned, H. H. Cunynghame (*Journal Society of Arts*, Dec. 11, 1903, vol. lii., p. 72; also *Engineering*, Dec. 11, 1903) has recently shown how greatly the efficiency can be improved by the adoption of better insulation.

Despite this lack of knowledge the measurement of thermal conductivities of such materials is by no means difficult to carry out, at any rate to within an accuracy of 2 or 3 per cent. C. H. Lees and J. D. Chorlton (*Phil. Mag.*, June, 1896, [5], vol. xli., pp. 495-503) have specially designed a simple apparatus for measuring the thermal insulation of bad conductors. We are much indebted to Dr. Lees, who very kindly lent the apparatus, and also gave much valuable advice in carrying out the experiments.

Measurement of Thermal Conductivities of Granular Materials up to 100° C.

All the substances dealt with have been either in the state of well-defined granular powders, or in some few cases where bricks have been examined, these were previously broken up and finely powdered. The apparatus of Lees and Chorlton was originally designed for round tiles or plates of material, but these have to be of uniform thickness and 11.4 c.m. diameter, and the shaping of bricks is not easily accomplished in the laboratory. A sketch of the apparatus is given in Fig. 1. It consists essentially of two thick metal discs between which the material is placed whose thermal conductivity has to be measured. The upper disc is surmounted with a steam jacket, whilst the lower one is allowed to cool by free conduction and radiation. Three thermometers are used, one to give the temperature of the upper, the second that of the lower disc; whilst a third gives the temperature of the surrounding air. The thermometers are inserted into radial holes drilled in the discs and thus denote their temperature with fair accuracy. When steam is passed through the steam jacket the temperature of the upper disc is raised to nearly 100° C., heat flows through the material experimented on, and thus raises the temperature of the lower disc above that of the surrounding air. The lower disc loses heat by conduction and radiation to the air. Eventually a steady state is reached, when this loss of heat is equal to the heat received through the material experimented on.

The following equation enables the thermal conductivity (K) to be calculated from the result of such an experiment provided h_1 , the external conductivity or "emissivity," has been previously determined:—

$$K = \frac{t_2 - t_1}{t_3 - t_2} \cdot b \left(h_1 + h_1' + \frac{\rho h_1}{2q} \cdot b \right);$$

where t_1 , t_2 , and t_3 are the temperatures indicated by the thermometers T_1 , T_2 , and T_3 respectively, and b denotes the thickness of the layer of powder.

The value of h_1 is determined in a separate experiment

* Read before the Faraday Society, July 3, 1905.

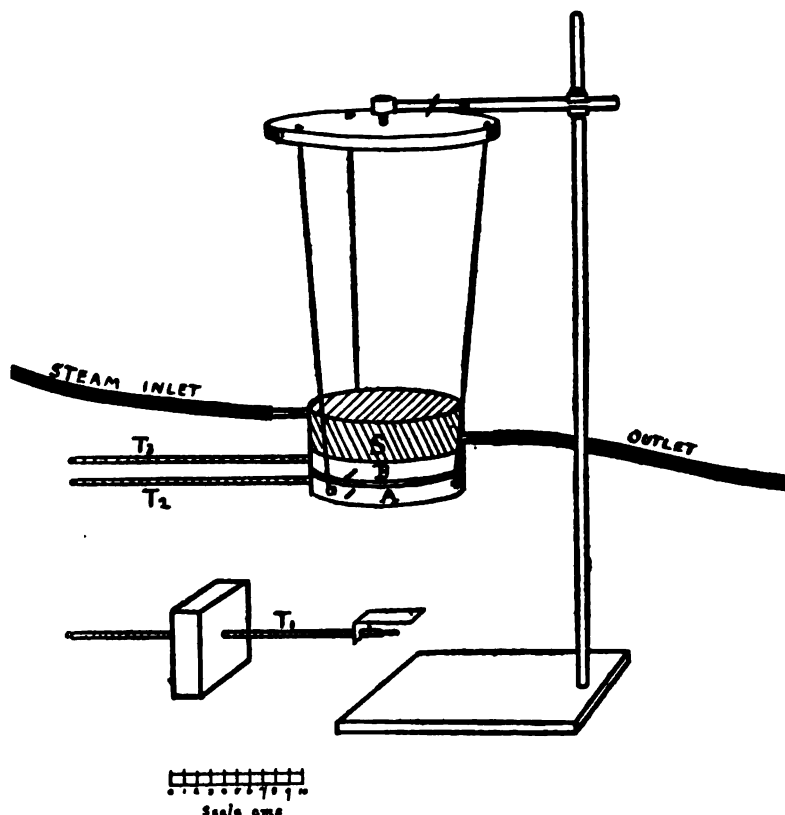


FIG. 1.—APPARATUS OF LEES AND CHORLTON FOR MEASUREMENT OF THERMAL CONDUCTIVITY OF BAD CONDUCTORS.

- A = Round disc of brass on which the substance under investigation is placed; it is suspended from a horizontal support by three strings. The disc is 11.4 c.m. diameter and 1.3 c.m. thick. The powders are kept in position by a thin ring of red fibre, which in the present work was about 0.36 c.m. high.
- B = Upper disc of brass of same dimensions as A. It is surmounted by the steam box s, which is covered with felt to diminish the loss of heat.
- A and B are provided with projecting pegs, the distance apart of which gives a measure of the thickness of insulating material.
- T₁ is a thermometer registering the temperature of the air; it is provided with a screen to protect it from radiated heat from the lower disc.
- T₂ and T₃ indicate the temperature of the lower and upper disc respectively, they are inserted into radial holes drilled in the brass.

from the rate of cooling of the lower disc at different temperatures.

In all the experiments here recorded the thickness was practically the same (0.360 c.m.), and as in nearly all cases the thermal conductivities were much of the same order, the term in the bracket was very nearly constant and equal to 0.00046.

Substance.*	Thickness in c.m.	Temperatures, °C			Conductivity. K.
		t ₂	t ₃	t ₁	
Sand. White Calais	0.360	98.4	81.0	18.2	0.00060
Carborundum (fine)	0.363	98.7	78.8	18.3	0.00050
Carborundum (coarse)	0.358	98.7	79.6	18.7	0.00051
Quartz "Enamel"	0.362	99.3	75.4	21.7	0.00036
Quartz (fused)	0.362	98.9	74.9	17.4	0.00039
Firebrick	0.363	98.7	69.2	20.3	0.00028
Retort graphite	0.363	100.0	76.6	19.6	0.00040
Lime	0.363	98.1	70.1	20.8	0.00029
Magnesia (fused)	0.356	98.7	78.6	20.0	0.00047
Magnesia, "Mabor" brick	0.360	99.7	80.0	18.8	0.00050
Magnesia, calcined Greek	0.365	99.3	78.3	20.4	0.00045
Magnesia, calcined "Veitsch"	0.366	99.7	73.9	20.0	0.00034
Magnesia, Pattinson's light calcined	0.363	98.0	58.5	19.7	0.00016
Kieselguhr (infusorial earth)	0.366	97.9	53.9	17.7	0.00013

* Most of these granular powders just passed through a sieve with 600 meshes per sq. c.m.

Relative Value of different Heat Insulating Materials at High Temperatures.

It is not advisable to choose a material suitable for furnace uses from the above data alone.

Firstly, it is always necessary to know the general effect upon the substance under investigation of such temperatures as are likely to be experienced. Several, even amongst those materials mentioned in the table, are unsuitable for subjecting to high temperature on account of the physical changes, such as shrinkage, which they undergo. Chemical action, especially oxidation, also renders many insulators unsuitable for a large number of purposes.

Secondly, having by such considerations excluded all unsuitable materials from the choice, it becomes necessary to compare the relative efficiency of those which remain under conditions more nearly approaching those experienced in practice.

The following experiments were carried out with a view to testing in as simple a manner as possible the behaviour of various refractory materials at comparatively high temperatures.

The method employed, although it does not directly lend itself to the accurate measurement of the absolute conductivities, at any rate offers a practical means for making comparative tests.

Description of Apparatus.

A modified form of electrically heated tube furnace was

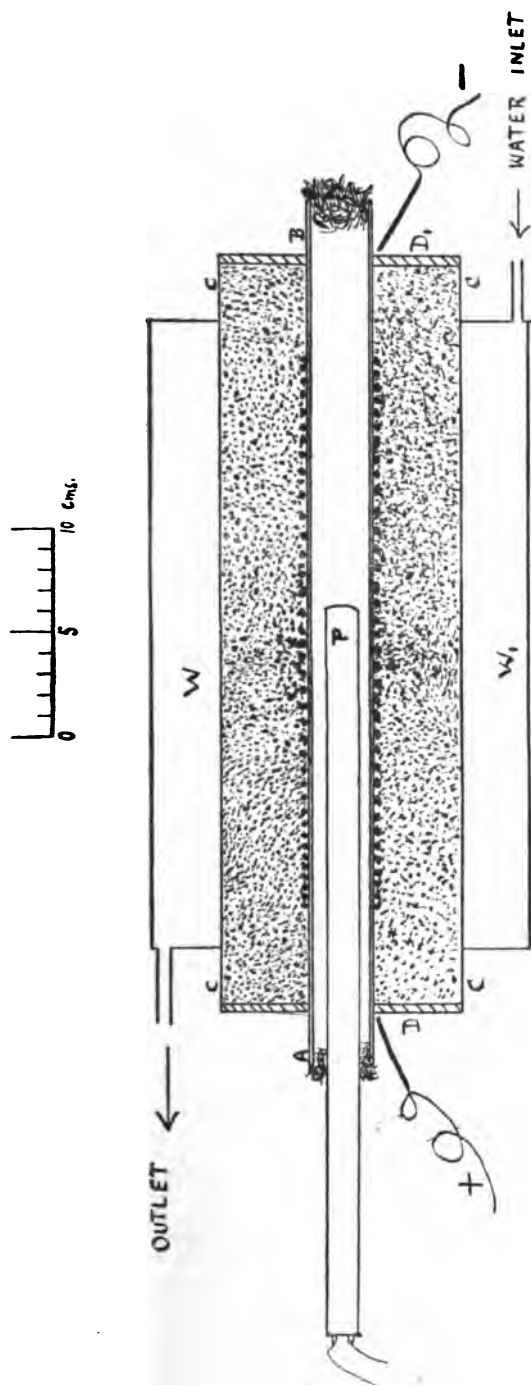


FIG. 2.—APPARATUS USED FOR COMPARISON OF HEAT INSULATORS AT HIGH TEMPERATURES.

A, B, Unglazed porcelain tube with heating coil of nickel wire wound on its central portion.
The porcelain tube is kept in position at the centre of the cylinder of sheet iron, C, C, C, C, by washers of asbestos card, D, D1.
W, W1 is the water jacket surrounding the cylinder C.
P is a thermo-electric pyrometer by which the temperature is indicated.
The granular insulating material under test fills the space between the porcelain tube and sheet-iron cylinder.

employed. An unglazed porcelain tube, with a heating coil of nickel wire, is supported at the centre of a cylindrical, water-cooled enclosure, the space between the heating coil and the inner wall of the enclosure being filled with the granular material under investigation. (See Fig. 2.) The electric energy expended in the wire is kept constant over a considerable period by careful adjustment of an external resistance and constant observation of a precision wattmeter. The temperature at the centre of the porcelain tube is noted at regular intervals, and from the observations a curve is plotted to show the relation between the rise of temperature and the time during which the heating has been in progress. The temperature of the water flowing through the external jacket was kept fairly constant; generally it varied some 2°C .

In such an experiment it would require a very long time for the temperature to attain a constant value. It was therefore found preferable, after the rate of increase in temperature had become rather slow, to reduce the power by a small but definite amount. Under these conditions the temperature falls, at first very rapidly, but soon reaches a constant value, or at any rate falls so slowly as to be almost negligible. It is from a comparison of the heating curves with different materials and the same expenditure of power, and particularly from the nearly horizontal portion of the curves with lower power expenditure, that valuable conclusions can be drawn.

The accompanying diagram (Fig. 3) illustrates some of the results obtained.

In the case of firebrick, carborundum, and sand, the preliminary heating was effected with 300 watts, and after the lapse of about two hours the power was reduced to 250 watts, being kept constant at this for a period of one and a-half to two hours, by which time the temperature had become almost constant. The curves for kieselsphur (infusorial earth) and light magnesia clearly show the very much smaller conductivity of these materials. (cf. F. A. J. FitzGerald, *Electrochemical Industry*, 1905, vol. iii., p. 55).

With these two substances the preliminary heating was effected with an expenditure of only 150 watts, but despite this the rise in temperature is more rapid than with any of the other materials mentioned.

Unfortunately, neither light magnesia nor infusorial earth can withstand any high temperatures for long without losing their efficiency to a considerable extent. Both substances exhibit large shrinkage at high temperature, and their chief uses are likely to be limited to external jacketing of furnaces lined with some more permanent but less good insulator.

To more thoroughly test the above method of comparing the relative efficiency of different materials at high temperatures, it was thought advisable to see what influence the preliminary heating might have on the results.

Two similar experiments were therefore carried out with the various substances. In the first case the preliminary stage of the heating was effected with 300 watts, in the second with 250 watts. In both cases the power was subsequently reduced to 200 watts, and then to 150. The results showed that in all those cases in which no permanent alteration is brought about in the materials under test, the horizontal portions of the curve are practically identical, whatever the preliminary treatment had been.

In earlier experiments, in which no water-cooling had been used to maintain constant the temperature of the outer jacket of the enclosure, some anomalous results were obtained.

General Conclusions.

The above results will, it is hoped, prove of value to those who have to deal with refractory materials. The subject seems to have been much neglected, considering that the thermal conductivity of such substances is the characteristic property which is really applied in their many uses.

Whilst bricks and generally jacketing materials for furnaces should be of low thermal conductivity, it is of no less importance to choose crucibles, retorts, and other con-

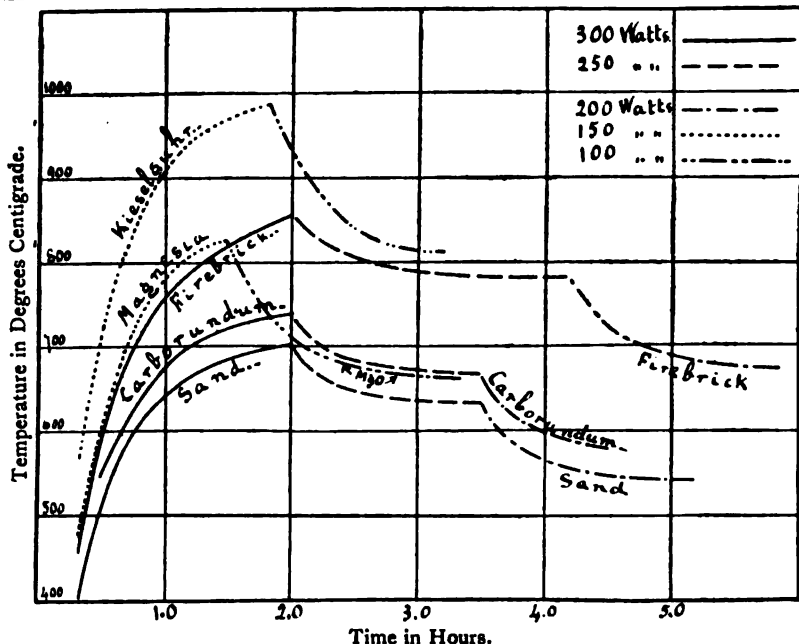


FIG. 3.—CURVES SHOWING RELATIVE INSULATING POWER OF MATERIALS.

taining vessels which are heated externally of as high conductivity as is feasible in conjunction with their other necessary qualities. Such methods as have been described are equally applicable to this latter case.

By a judicious use of the different materials and a stratified form of construction, it should be possible usefully to employ such excellent insulators as infusorial earth without risk of the damage which is inevitable if they be permanently subjected to too high a temperature.

The above experiments were carried out in the Physical Laboratories of the Manchester University.

THE USE OF COPPER IN DESTROYING TYPHOID ORGANISMS, AND THE EFFECTS OF COPPER ON MAN.*

By HENRY KRAEMER.

(Concluded from p. 45).

The Effects of Water Treated with Copper on Man.

WHILE it has been conclusively shown that exceedingly minute quantities of copper are toxic to typhoid organisms, still the question is raised by some as to the toxic effects on man when copper or its salts is used in the purification of drinking-water. In commenting on a paper of mine on "The Efficiency of Copper Foil in Destroying Typhoid and Colon Bacilli in Water," a reviewer writes as follows (*Medical Notes and Queries*, March, 1905, i., No. 3, p. 38):—"While recommending the use of copper foil for the purification of drinking-water, the writer adduces no proofs as to freedom from toxic effects when water so purified is taken into the system over a considerable period of time." My reason for not taking up the pharmacological phase of this question heretofore has been that my own experiments in the consumption of water treated with copper foil did not extend over a sufficient period of time to warrant me in making any statements in regard to the effects of water so treated. Then, too, I felt that the statements of pharmacologists and physiologists were con-

clusive as to the probable harmlessness to man of copper when used in the proportions necessary to purify water containing typhoid organisms. But since there seems to be some objection in certain communities to the drinking of water treated with copper, I have deemed it advisable to give my own experience in connection with this subject.

For over six months all of the drinking-water consumed in my home has been treated with copper. A strip of copper foil, or sheet copper, 9 inches square, is placed in a vessel containing from 3 to 4 quarts of water and allowed to remain from four to eight hours. The foil is first cleaned with powdered pumice, and retains its lustre for weeks unless the water contains a considerable quantity of sediment, and provided the quantity of water is renewed immediately each time upon drawing off the sterilised water. On account of the varying amounts of sediment we find it desirable to filter the water before treating it with the copper foil. Up to this time no ill effects have been noted from drinking the water so treated, and, in fact, our general health may perhaps be said to be better than usual, in that we have not had to consult a physician during this time. Another interesting observation is that the water being more palatable than boiled water, we consume larger quantities, which possibly has some influence on the general bodily condition.

Believing, as I have already indicated, that many vegetables may also be a source of infection, we take the precaution either to wash the vegetables to be eaten raw in copper-treated water, or to place them, particularly in the case of lettuce and celery, in a vessel of water along with a strip of clean copper foil and allow them to remain from two to four hours with occasional agitation.

The use of copper vessels would be more convenient, but of course is more expensive. I have also thought that water-pitchers and tumblers might be partly lined with pieces of copper foil.

I may say in addition that I know of a number of families who have been using copper-treated water for even a longer period of time without any untoward effects.

The Elimination of Copper from Water.

Nägeli (*loc. cit.*) discovered during the course of his experiments that a solution of copper that was toxic to

* From the *American Journal of Pharmacy*, vol. lxxvii., No. 6.

Spirogyra could be rendered harmless by the introduction of a number of more or less insoluble substances. Among those which he used for this purpose were the following: Sulphur (either roll or flowers), carbon (either graphite or soot), coke, coal, peat, black oxide of manganese, starch, cellulose (either as Swedish filter-paper, or cotton, linen, or wood fibre), silk, wool, stearic acid, paraffin, gum, dextrin, egg albumin, glue. True and Oglevee (*Botanical Gazette*, 1905, xxxix., pp. 1-21) have studied the influence of insoluble substances on the toxic action of poisons in solution, and have not only confirmed Nägeli's observation, but have shown that sand and powdered glass have the property of reducing the toxicity of solutions of copper. Moore and Kellerman have shown in their recent Bulletin the relative decrease of the toxicity of copper sulphate solutions according to the amount of organic matter present, the amount of carbon dioxide dissolved in the water, or the temporary hardness of the water.

In addition, the copper is absorbed by the organisms which are killed, and is thus eliminated. It is therefore apparent that there are a number of ways by which the copper is removed from solution and the toxicity of solutions containing it lessened.

In the case of reservoirs treated with copper it is likely that none or very little copper remains in solution for any considerable period of time. By a combination of factors, such as (a) absorption by the organisms that are killed as well as by other organic matter; (b) by the formation of insoluble compounds with various inorganic salts; and (c) by adsorption by various insoluble materials, the copper is removed, so that by the time the water reaches the consumer there is probably no copper in solution, and the insoluble copper, if present, is necessarily more or less inert. Furthermore, I am of the opinion that there is more copper in solution in home-filtered water which has been treated with copper foil than in the water which reaches the consumer after treatment of a large reservoir with copper sulphate in the quantities proposed by Moore and Kellerman for the purpose.

The Occurrence of Copper in Foods.

Among the other inorganic constituents which occur normally in the animal organism is copper, and its occurrence is so constant as to be spoken of as "normal copper." It is not known, however, what part, if any, it plays in metabolism. The amount normally present varies with the food and with the individual. There is considerable data showing that the amount of copper in vegetables varies according to the amount of copper present in the soil, and owing to its wide distribution in soil, it is found in many plants. It is therefore naturally present in many foods, and may run as high as 0.560 grm. per kilogram. of dried substance, or even 1 part in 175 parts, in plants growing near copper works, as shown by Lehmann (*"Hygienische Studien über Kupfer IV."* *Arch. f. Hygiene*, 1896, xxvii.).

In addition, copper is added to many foods to enhance their appearance. The custom of greening vegetables has been followed in a commercial way for over fifty years, and laws are being enacted defining the limit of copper which is permissible in food materials. The Swiss and Italian Governments allow a quantity of metallic copper not to exceed 100 m.grms. per kilogram. (or 1 part in 10,000) in vegetable preserves. In France the question of re-greening vegetables by means of copper sulphate has received careful attention, and while the practice was prohibited by law in 1853, this prohibitory law was repealed in 1889. According to Leach:—"Examination of a large number of brands of canned vegetables greened by copper, as bought in Massachusetts, showed that the amount varied from a trace to 2.75 grms. per can, calculated as copper sulphate. . . . In the Massachusetts market labels like the following are not uncommon: 'This package of French vegetables contains an equivalent of metallic copper not exceeding three-fourths of a grain.'" In Pennsylvania the law "permits articles of vegetable

food to contain as much as $\frac{1}{2}$ of 1 per cent of metallic copper," or 1 part to 5000 parts of food.

The Effects of Foods containing Copper on Man.

Being without any other reliable data as to the physiological effects of copper on man, save as a medicine, we naturally turn to the foods containing copper for evidence as to the effects of copper on man. The question has been repeatedly discussed before the courts, particularly in England, and the studies of Lehmann and others in Germany have contributed materially to an elucidation of the problem.

It is probable that the copper naturally occurring in plants is in a condition different from that found in food products which have been artificially treated with copper. That is, in the former case the copper is in a labile condition, and therefore more assimilable, while in the latter case the compounds formed by the combination of the copper with the proteids and chlorophyll are less soluble, and the copper is extracted only in part by acids of the strength of the gastric juice. According to Tschirch and Brandel (quoted by Dr. Smith in Buck's "Handbook of Medical Sciences"), the copper in these more or less insoluble compounds is but slightly toxic. "From experiments with copper proteid Filehne concluded that an amount equivalent to 0.500 grm. of copper per day would produce no notable result in an adult" (Buck's "Handbook of Medical Sciences").

"Contrary to the earlier teachings, recent observations tend to the view that there is no chronic copper poisoning comparable with that of lead. According to this view the long continued ingestion of minute doses of copper by the stomach and the exposure to absorption in handling and working the metal, are not capable of producing systemic poisoning. This view is based largely upon the negative results obtained in feeding experiments with man and the lower animals, and in the therapeutic use of copper salts" (*loc. cit.*).

Galippe had all of the foods which were used in his family for fourteen months cooked in copper vessels, and reported that no trouble was experienced. Dr. Smith (*loc. cit.*), in discussing the use of copper utensils for cooking purposes, says:—"It seems impossible that enough copper could be present in food which would be eaten at one time to produce serious acute poisoning as has been frequently supposed, especially as the presence of as much as $\frac{1}{2}$ a grm. of copper in 1 kilogram. of liquid food would produce a marked metallic taste."

Pasteur says (*Ann. d'Hyg.*, publ. Par., Series 3, iii., p. 204, March, 1880):—"In regard to the toxicity of copper salts, it may be said it is almost impossible to take a dose large enough to produce death, both from their horrible taste and from the violent vomiting which they produce. In small quantities the taste is not perceptible, and the salts are not only tolerated but absorbed. Workers in copper are often completely saturated with the metal, but do not suffer from it. Experiments on animal and human subjects have never given a worse result than vomiting or a temporary fit of colic. Copper normally exists in the human body. It gains entrance from various foods and drinks in the absence of all adulteration. It accumulates to a certain extent, but injury from this accumulation is unknown. In the sample submitted, copper exists to an extent varying between 16 and 45 m.grms. per kilogram. . . . The quantity found does not constitute a danger to health."

Conclusions.

1. It is pretty well established that the typhoid organism is disseminated not only through water, but also through air and food, and may retain its vitality for a considerable period of time.

2. Typhoid organisms in water are eliminated by filtration, boiling, and certain biochemical methods. Of the latter, the use of copper, as proposed by Moore and

Kellermann, is probably the most efficient and at the same time most practicable.

3. While exceedingly minute quantities of copper in solution are toxic to certain unicellular organisms, as bacteria, it is safe to assume that the higher plants and animals, including man, are unaffected by solutions containing the same or even larger amounts of copper.

4. There being a number of factors which tend to eliminate copper from its solutions, it is hardly likely that there would be any copper in solution by the time the water from a reservoir reached the consumer if the treatment of the reservoir were in competent hands.

5. Many plants contain relatively large quantities of copper, and when these are used as food some of the copper is taken up by the animal organism, but there are no records of any ill effects from copper so consumed.

ZINC DUST.

By A. B. STEVENS.

BEFORE using zinc dust in some experiments upon the gum obtained from Japanese lac I wished to be sure that it was free from nitrogen; I therefore subjected the zinc dust to the following tests, the results of which may be of interest to those who frequently use it in connection with organic substances.

When heated with potassium hydroxide it formed ammonia. When heated alone it also gave off ammonia. This led to the belief that nitrogen in some form had been absorbed from the atmosphere, and might be removed by heat. A small quantity was therefore placed in a loosely covered crucible, and strongly heated for half an hour. When cold it was tested for nitrogen by heating with potassium hydroxide. Its vapours rapidly changed litmus-paper from red to blue. Upon the suggestion of Professor Tschirch a sample was thoroughly washed with water acidulated with hydrochloric acid, but this failed to completely remove the nitrogen.

As zinc dust is manufactured by heating zinc oxide with coal, it was believed that part of the nitrogen might consist of condensation products from the coal. Therefore a sample was placed in a long tube and percolated with ether. The ether when evaporated left a yellow, non-saponifiable oil, with an odour and fluorescence similar to petroleum. The oil, when heated with dry potassium hydroxide, gave off alkaline vapours, and the zinc in the percolator was still found to contain nitrogen. The greater portion of the oil appeared to be removed with the first portion of ether, but after continued percolation the ether left a residue upon evaporation, and it was evident that a much larger amount of ether was necessary for complete exhaustion; therefore a smaller sample, from a can of zinc dust which had been in the laboratory for more than ten years, was treated with ether in the same manner, and the powder tested from time to time. After using a large amount of ether the zinc was practically free from nitrogen, yet by taking a large amount of the zinc and heating with potassium hydroxide in a tube partially closed at the top so that all of the vapours came in contact with the litmus-paper, the colour was slightly changed, thus showing a mere trace of nitrogen. This sample was then allowed to stand in an open flask for a few days, when it gave a decided ammonia reaction, thus showing that zinc dust rapidly absorbs nitrogen from the air.

The fact that only a portion of the nitrogen in zinc dust is removed by heat indicates that the nitrogen is present in more than one form. This theory is also supported by the following experiments:—

A fresh sample of zinc dust was washed with water, the washings giving a decided ammonia test. The washing was continued as long as traces of nitrogen could be detected in the washings. It was then treated in the same manner with very dilute hydrochloric acid. By adding

potassium hydroxide in excess to the acid solution and allowing to stand a few minutes until the precipitate settled, decanting the clear solution and boiling, the vapours gave the odour of ammonia and rapidly changed litmus from red to blue. Washing with acid was continued until the washings no longer gave a test for nitrogen. The zinc was then washed with water until free from acid, and rapidly dried in a drying oven, and at once extracted with ether, the ether evaporated and tested for nitrogen as above. Nitrogen was found to be present, though not in as large amounts as in the oil from the first sample examined, which was, however, directly treated with ether.

Three samples were examined: one from a large closely covered can which has been in use in the laboratory as above stated; another from a glass bottle which has been in the museum about fifteen years, and a third which was ordered by Professor Oesterle for these experiments. Practically the only difference found in the three samples was that the oil from the fresh sample was decidedly yellow, while that from the laboratory sample was somewhat lighter, and that from the museum sample was colourless.

Dr. V. Steger ("Metallimpfe in Zinkhütten," "Chem. und Chemischtechnischer Vorträge") gives the results of several analyses of zinc dust, some of which contain considerable insoluble residue consisting principally of carbon. To determine to what extent this was present, a large amount of zinc dust was treated with hydrochloric acid. At first the reaction was rapid, but after a time ceased. The solution was decanted and fresh acid added, but as the reaction was very weak the mixture was heated. Even then a large amount remained undissolved. A few drops of copper sulphate solution were added and digested for several days, but a large amount remained insoluble. This was washed with water until free from acid, dried, and percolated with ether, which upon evaporation left a colourless oil. Upon removing the ether the zinc dissolved without difficulty in hydrochloric acid, conclusively proving that this sample contained no carbon, and that the insolubility was due to the presence of the oil.—*American Journal of Pharmacy*, lxxvii., No. 6.

NOTICES OF BOOKS

Twenty-ninth Annual Report of His Majesty's Inspectors of Explosives; being their Report for the Year 1904. London: Darling and Son, Ltd., 1905. Pp. 241.

DURING the year 1904 there have been two modifications of the law, viz., Order of Secretary of State, No. 4 (a), regulating the deposit of explosives in dust-bins, &c., for conveyance as rubbish, and Order of Secretary of State, No. 7, consolidating and re-arranging the regulations in regard to the packing of explosives for conveyance.

We are glad to note that the Inspectors have found no reason to complain of any falling off in the general conditions of factories and magazines, and that they have not had occasion during the year to institute legal proceedings for any irregularity brought to light by their inspections. The occupiers of factories and magazines have invariably shown perfect readiness to remedy such defects as have been pointed out, and the managers themselves, in many instances, have introduced improvements tending towards greater safety.

The number of deaths from accidents by fire or explosion in the manufacture of explosives is considerably above the average for the past ten years, viz., 13, compared with 7.5. Still this number of deaths is not excessive, and will compare favourably with the death-rate in other dangerous trades.

The total number of factories under continuing certificate or license is 148, being an increase of 1 during the year; of the above total, 4 factories are under notice of temporary disuse.

During the year there have been 19 explosives added to the authorised list, and 17 added to the authorisable list.

It will be seen on reference to Dr. Dupré's report, Table I., that out of 417 samples examined by him 66 were rejected.

During the year, 241 visits to factories have been made; the number of accidents occurring during this period is 42, causing 13 deaths, and injuring 29 persons, but it is as well to point out that a considerable proportion of the total number consists of accidents of an unimportant character, while in the case of some of the accidents by which persons were injured the injury was slight.

Several cases of the illegal manufacture of blasting cartridges by miners in their houses were brought to light by accidents during the year, and three other cases of the manufacture of unauthorised explosives were found.

The number of magazines under continuing certificate and license is now 425, being an increase of 5 on the previous year, and it is satisfactory to find that there has been no case of accident by fire or explosion in connection with any magazine during 1904.

The amount of foreign blasting explosives containing nitroglycerin imported during the year shows a slight falling off compared with 1903, the figures being 2,244,723 lbs. and 2,330,582 lbs. respectively; while the corresponding figures for blasting explosives not containing nitroglycerin are 252,606 lbs. and 168 lbs. and 2 cases respectively; a large proportion of the blasting explosives imported into England was for transhipment to other countries, viz., 1,759,652 lbs. out of 2,497,329 lbs.

During the year experiments were carried out at the Home Office Testing Station with the object of obtaining comparison between detonators charged with different compositions; details of these experiments are given in Appendix O (1). Other experiments were made to ascertain the liability to ignition by electric spark of dry nitro-cotton in a fine state of division. Only negative results were obtained.

A detailed account is also given of a series of experiments carried out in Belgium to determine the distances at which the explosion of varying quantities of dynamite would be felt in the open air; the results are given on pp. 63 and 64.

On October 24th, a new Order in Council was made, altering and extending the quantity of carbide of calcium which might be kept without a license. Originally the amount was restricted to 5 lbs., but it has now been increased to 28 lbs., provided notice is given to the local authority and certain precautions are observed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 1, July 3, 1905.

Camphoacetic and β -Camphopropionic Acids.—A. Haller.—The author's researches show that though cyanosodo-camphor—except for certain exceptions which have been noticed—always behaves as an enolic molecule, methyl camphocarbonate can be considered as a β -ketonic body which gives carbon products when its sodium derivative is treated either with alcoholic iodides or sodium ethers. Owing to this property of camphocarbonic ether, its superior homologues can easily be prepared, using as an intermediary the double ethers to which the carboxymethyl group can be raised.

Synthesis of the Three Tertiary Dimethylcyclohexanols and the corresponding Hydrocarbides.—P. Sabatier and A. Mailhe.—Using the three cresols, the authors prepare ortho-, meta-, and paradimethylcyclohexane, and they find that the carbides thus obtained have very similar properties to those of the three dimethylcyclo-

hexanes which MM. Sabatier and Senderens prepared some years ago by the direct hydrogenation of the three xylenes. As for these latter carbides, the boiling-point of the ortho-derivative is much higher than that of the meta- and para-derivatives. The contrary is true of the corresponding alcohols, and also of the phenolic bisubstituted derivatives.

Preparation of Binary Compounds of Metals by means of Aluminium.—A. Colani.—Aluminium powder may be employed for the preparation of binary compounds in the absence of the electric furnace. Unfortunately, however, the products obtained generally contain a little aluminium and often iron also.

Constitution and Properties of Aluminium Steels.—Leon Guillet.—The author proves that aluminium has no important action on the mechanical properties of steel when it is present in quantity less than 2 per cent. Up to 15 per cent the aluminium enters into solution with the iron. The iron-aluminium solution thus formed does not dissolve carbon. It also takes a granular form, which explains the fragility of certain steels. Finally, in steels containing a large proportion of aluminium free martensite is found.

Compounds of Hydroferrocyanic and Sulphuric Acids. Sulphono-substitution in the Molecule of Complex cyanides. The Oxyferrocyanides.—Paul Chrétien.—The author prepares various compounds of hydroferrocyanic and sulphuric acids, and finds these substances decompose very easily in damp air, hydroferrocyanic acid being reproduced. The action of alkalis on the compound FeCySO_2 is very remarkable, as it shows the absence of hydrogen in the molecule.

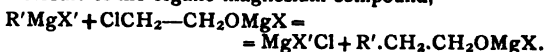
γ -Acid Aldehydes.—E. E. Blaise and A. Courtot.—The authors describe the preparation of the γ - $\alpha\alpha\beta$ -trimethyl and $\alpha\alpha$ -dimethyl- β -phenyl acid aldehydes. These two bodies are solid, and melt, the first at 63° and the second at 131° .

Synthesis of the Lactone of Erythric Acid.—M. Lespieau.—The lactone of erythric acid ($\text{C}_4\text{H}_6\text{O}_4$), which the author succeeds in synthesising, melts at 91° . It is very soluble in water and insoluble in ether.

New Method of Synthesis of Mono- and Poly-atomic Alcohols.—V. Grignard.—The author's method consists in acting with the mixed organo-magnesium compounds of formula RMgX on the halogen derivatives of mono- or poly-atomic alcohols. Considering the preparation of glycol monochlorohydrine the reaction takes place in two phases,—



The complex thus obtained is capable of reacting on a new molecule of the organo-magnesium compound,—



β -Decahydronaphthyl Ketone and β -Decahydronaphthylamine.—Henri Leroux.—The author describes the preparation of various compounds prepared from the alcohol β -decahydronaphthol, which substance he investigated in a previous research.

New Derivatives of Mesoxalic Ethers.—Ch. Schmitt.—The author prepares the bisanilide of methyl mesoxalate, $(\text{CH}_3\text{CO}_2)_2\text{C}(\text{NHC}_6\text{H}_5)_2$, the bisanilide of ethyl mesoxalate, $(\text{C}_2\text{H}_5\text{CO}_2)_2\text{C}(\text{NHC}_6\text{H}_5)_2$, and the orthotoluide of methyl mesoxalate, $(\text{CH}_3\text{CO}_2)_2\text{C}(\text{NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2$, and investigates their properties.

Sparteine and its Action on Ethyl Iodide.—Charles Moureu and Amand Valeur.—During the action of ethyl iodide on sparteine, sparteine iodohydrate is formed, and two isomeric iodoethylates, either in a free state or combined with hydriodic acid.

Densities of Carbonic Anhydride, Ammonia Gas, and Nitrogen Peroxide.—Philippe A. Guye and Alexandrie Pintza.—The authors find the mean values of the densities of the three gases, CO_2 , NH_3 , and N_2O , to be 1.9768, 0.7708, and 1.9774 respectively.

Thermo-chemistry of Neodymium.—Camille Matignon.—The author's investigations on the thermo-chemistry of neodymium show that this metal, and consequently the allied metals of the rare earth group, must be placed, from the point of view of their chemical affinity for the other elements, between the alkaline-earth metals and magnesium.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 7, 1905.

Methylazide.—Otto Dimroth and Wilhelm Wislicenus.—To prepare methylazide, sodium nitride (prepared by the action of ammonia gas upon sodium at 290–350° in a covered nickel vessel, or by the action of nitrous oxide upon sodium amide at 190°) is dissolved in water, the ammonia still present in the strongly alkaline liquid is completely expelled by a current of steam, and the solution is gently heated upon a water-bath in a flask fitted with a reflux condenser and a dropping funnel; dimethyl sulphate is then introduced, drop by drop, when methylazide is formed. It is purified and dried by passing through a U-tube filled with granulated calcium chloride and soda-lime, and heated to 25° to 30°, and is collected in a second U-tube, which is surrounded by a cooling mixture. Methylazide is a colourless liquid with a somewhat ethereal unpleasant odour, recalling that of hydrazoic acid. The combustion of the compound (performed with special precautions owing to its explosiveness) shows that the empirical formula is CH_3N_3 . The boiling-point is 20–21°, and the explosion temperature lies considerably above 500°.

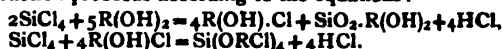
Quantitative Determination of Halogens in Chlorates, Bromates, and Iodates.—P. Jannasch and A. Jahn.—Red fuming nitric acid readily reduces potassium bromate and potassium chlorate quantitatively to bromide and chloride respectively. In the former case the flask in which the reaction takes place must be connected with a long Liebig's condenser to prevent the escape of bromine. Potassium iodate is not reduced quantitatively at ordinary pressures, but under increased pressure continued heating of it with silver nitrate and red fuming nitric acid causes the formation of the theoretical amount of silver iodide. Ordinary concentrated nitric acid when heated under pressure with chlorate and bromate will reduce them quantitatively, but not the iodate. This action of nitric acid is to be explained by the liberation of the halogen acid, which is then decomposed very readily in the case of chloric acid, and with great difficulty in the case of iodic acid. Hydrogen peroxide has no action in alkaline solution; in presence of nitric acid it reduces both chlorates and bromates, but not iodates. Hydrazine sulphate reduces potassium iodate and bromate very readily in alkaline solution, while the chlorate is scarcely attacked; formic acid behaves similarly, but with the iodate reduction proceeds until metallic iodine is separated. Grape-sugar and acetic acid under pressure yield the theoretical amount of silver chloride from chlorates. Reduction with hydroxylamine sulphate gave the best results; in acid solution the action is much stronger than in alkaline, metallic iodine being separated from iodates. Thus with chlorates, when the action is feeble, the reduction is best performed in acid solution, while with iodates and bromates the preference is to be given to ammoniacal solution.

Organic Silicon Compounds.—Fritz Taurke.—From silicon chloroform and *N*-propyl, isobutyl, and isoamyl alcohol in absence of moisture, the corresponding esters, $\text{SiH}(\text{OR})_3$, are formed, hydrochloric acid escaping. With aliphatic chlorides, silico chloroform and metallic sodium give the following reaction:—



This behaviour is noteworthy in view of the fact that with aromatic chlorides or bromides the tetra alkyl compounds are formed. With glycols silicon chloride first yields a glycol chlorhydrine, which then reacts like a monatomic

alcohol with more silicon chloride, giving the simple chlorinated alkyl ester of silicic acid of the formula $\text{Si}(\text{ORCl})_4$. It is best to employ, in the first instance, only as much silicon chloride as will yield the chlorhydrine, which is purified by distillation under normal pressure. More silicon chloride is then added to it slowly, and the reaction proceeds according to the equations:—



Simultaneously, white masses separate out; these were at first taken to be silicic acid, but on further examination were found to have a constant composition of 2 molecules of SiO_2 to 1 molecule of glycol. They may be a crystal alcohol, $2\text{SiO}_2\cdot\text{C}_2\text{H}_4(\text{OH})_2$, or else an acid ester of meta-silicic acid of formula $\text{SiO}(\text{OH})\cdot\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{SiO}\cdot\text{OH}$.

Action of Inorganic Compounds upon Optically Active Polyvalent Alcohols and Oxyacids.—Hermann Grossmann.—The salts of lead and bismuth are able, in presence of alkali hydroxides by substitution of atoms of hydroxyl hydrogen, to enter into the molecule of the higher alcohols and oxyacids, thereby causing extraordinarily great alterations in the specific rotation. The magnitude of the alteration varies very much in the mono-, di-, and tri-saccharides, which may perhaps throw some light upon the constitution of the polysaccharides. Alkaline lead solution, unlike uranium, tungsten, molybdenum, and boron compounds, reverses the direction of the rotation compared with that of the aqueous solution of the optically active compound. It was found that the action of lead acetate upon glucose in presence of sodium hydroxide caused a considerable increase in the specific rotation; in the case of fructose the rotation was turned from left to right. The occurrence of a maximum of rotation to the right when the molecular proportions were $2\text{C}_6\text{H}_{12}\text{O}_6 : 3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, and the subsequent formation of complexes richer in lead, show that different lead fructoates exist in the solution; these the author is endeavouring to isolate. Bismuth nitrate increases the rotation of mannite. A specimen of ammonium titanium tartrate showed the following peculiar behaviour:—In concentrated solution the rotation is towards the left; it decreases with increasing dilution till finally it becomes a dextrorotation, and this continually increases as the dilution increases. Such behaviour has never before been observed with salts of *d*-tartaric acid, and proves the great complexity of the compound.

Reduction of Tetrathionate to Sulphite by Arsenite and Stannite.—A. Gutmann.—On evaporating solutions of sodium arsenite and tetrathionate over sulphuric acid, sulphite, monosulphoxyarsenate, and tertiary sodium arsenate are obtained. No sodium sulpharsenate nor disulphoxyarsenate is formed. One molecule of tetrathionate always gives rise to 1 molecule of arsenate, decomposing according to the equation $\text{S}_4\text{O}_6 = \text{O} + \text{S}_2 + 2\text{SO}_2$. Sodium stannite reduces tetrathionate in alkaline solution to sulphite, sulphostannate and stannate being formed at the same time; under some experimental conditions some stannous sulphide is obtained.

Ketenes.—Hermann Staudinger.—The author has succeeded in isolating a substance of the formula $(\text{C}_6\text{H}_5)_2\text{C}:\text{CO}$, belonging to the hitherto unknown type $\text{R}_2\text{C}:\text{CO}$, to which he has given the name ketene. Diphenyl ketene is prepared by gently heating diphenyl-chloroacetyl chloride with zinc turnings and ether; the zinc chloride formed is precipitated with petroleum ether, and on distilling off the solvents the ketene remains behind as a brown oil. Diphenyl ketene is very reactive, and is oxidised when exposed to the air. In many respects its behaviour resembles that of the analogous isocyanic acid ester, $\text{RN}:\text{CO}$. With water the ethereal solution gives diphenyl acetic acid. With perfectly dry chlorine it yields diphenyl acetyl chloride, but if any moisture is present in the chlorine diphenyl acetic acid ethyl ester is formed. In cold benzene solution it is far more stable towards water than in ethereal solution.

MISCELLANEOUS.

The Paper Makers' Directory of all Nations.—We have just received this useful Directory for the year 1905; it is published by Messrs. Dean and Son, Limited, and contains all the principal paper, pulp, and board mills of the world. The work is alphabetically arranged throughout according to countries; the mills—some 5000 in all—being again set out under each country in a similar manner, and at the end of every section a classified list of the mill productions is given. Many useful hints are included, and the names of cardboard and paper box manufacturers, as well as those of china-clay dealers, have been added, so that this, the fourteenth, edition has been further increased by the addition of 20 pages.

Merck's Annual Reports, Vol. xviii., 1904.—These Reports are now so well known that little comment on their excellence is needed. They are widely appreciated and consulted as books of reference on pharmacology and therapeutics. Not only are Messrs. Merck's own new products specially mentioned, but the same treatment is unstintingly extended to interesting and valuable preparations originating from other sources. The present volume consists of 250 pages, and is sent free to medical men and others interested, on application to the London office at 16, Jewry Street, E.C.

Institute of Chemistry of Great Britain and Ireland.—Pass List of the July Examinations.—Of 19 Candidates who entered for the Intermediate Examination, 12 passed:—J. W. Agnew, H. G. Dale, James Dick, junr., W. P. Hayworth, I. M. Heilbron, R. F. Innes, S. Judd Lewis, A. J. C. Lickorish, F. L. Okell, R. P. Page, H. J. B. Rawlins, B.Sc. (Lond.), and D. R. Wood. In the Final Examination for the Associateship (A.I.C.), of 5 examined in the branch of Mineral Chemistry, 3 passed:—J. B. Hoblyn, Assoc.R.C.Sc. (Lond.), G. W. James, B.A. (Oxon.), and H. H. Kingdon, B.A. (Oxon.); of 6 in Organic Chemistry, 4 passed:—A. W. Bain, B.A., B.Sc. (Lond.), T. W. Cheke, J. Stuart Hills, and D. F. Twiss, M.Sc. (Birm.); and of 9 who entered in the branch of the Analysis of Food and Drugs and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following 4 passed:—R. W. Blair, Assoc.R.C.Sc.I., P. H. Carpenter, J. A. Goodson, and S. Summerson, B.Sc. (Lond.). One Candidate passed an Examination for the Fellowship (F.I.C.):—E. F. Harrison, B.Sc. (Lond.). The Examiners in Chemistry were Mr. W. W. Fisher, M.A., F.I.C., of Oxford, and Dr. G. G. Henderson, M.A., F.I.C., of Glasgow. The Examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A., M.B., F.R.S., F.I.C., of Cambridge.

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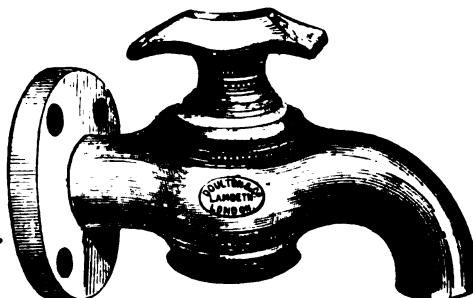
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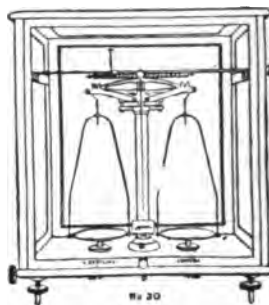
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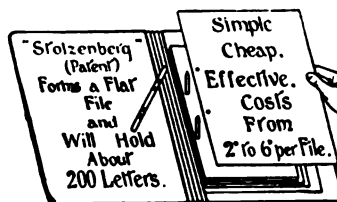
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THE CHEMICAL NEWS.

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WEATHERED HAY.

By W. F. SUTHERST, Ph.D., F.I.C.

DURING our haymaking period we were interrupted once by wet weather, which gave me the opportunity of finding out what effect the rain had on the constituents of the hay, with regard to their removal. A portion of the hay in the field, consisting principally of rye-grass, was protected from the rain, which lasted interruptedly for two days, and was then exposed to the sun with the rest. When dried it was analysed for the following constituents:—Moisture, albumenoids, carbohydrates, fibre, and ash.

The albumenoids were found by the Kjeldahl method, using a drop of mercury to hasten the reaction; the resulting nitrogen found being multiplied by 6.5. Fibre and carbohydrates, the latter by difference, by boiling a sample first with 5 per cent H_2SO_4 , then with 5 per cent KOH, removing the carbohydrates and albumenoids respectively.

The following results were obtained:—

	Water.	Albu- menoids.	Carbo- hydrates.	Ash.	Fibre.
Ordinary hay	15.65	16.52	39.14	5.43	28.91
Weathered "	12.75	14.58	37.14	4.96	33.32

All the constituents are calculated on dry matter.

It will be seen from the above results that first of all there is less water in the weathered hay; this seems at first curious, but it may be explained that the gummy substance in hay, which would be the first to be washed out, is hygroscopic, and attracts atmospheric moisture, whilst in the weathered portion this property would be present in a less degree.

The loss of two parts (14 per cent of total) of the nitrogenous substances is not so serious as might be expected, since the soluble nitrogenous bodies would be the amido-compounds, whose food value is very small; the more valuable albumenoids, being less soluble, remaining behind. The ash is of course less, since every part of hay contains ash, and the fibre being quite insoluble in water is undisturbed.

The Agricultural College, Tamworth.

THE ESTIMATION OF THE SILICA IN SUB-CARBONIFEROUS LIMESTONE.

By NICHOLAS KNIGHT.

THE specimen of the subcarboniferous limestone used in this work was obtained from a quarry near Bedford, Indiana, and it is known locally as the Bedford limestone. It is a light coloured rock, fine grained in texture, and it is widely used and favourably regarded as a building material.

The amount of residue insoluble in hydrochloric acid, which proved to be mainly silica, was determined by three different methods as follows:—

Method 1.—A grm. of the fine powder was placed in a small beaker covered with a watch-glass. Dilute hydrochloric acid was added, and the contents of the beaker gently heated to boiling. After standing a short time, the undissolved portion was filtered off, and the weight determined.

Method 2.—A grm. of the powder was placed in a porcelain evaporating dish, and while covered with a watch-glass, dilute hydrochloric acid was added. It was

left on the water-bath until effervescence ceased, the accumulations on the watch-glass were rinsed off, and the evaporation continued until crystals began to appear. Then as the evaporation went forward, the substance was stirred with a glass rod until a fine dry powder resulted. This was moistened with concentrated hydrochloric acid, and left on the water-bath for a few moments. Dilute hydrochloric acid and water were added, and after standing a short time the insoluble residue was filtered off, dried in the air-bath, and its weight determined. The insoluble residue was obtained three different times by each of the two methods, varying the weight of the original amount taken. The results were as follows:—

	Method 1.	Method 2.
(a) With 1 grm. substance..	0.54 per cent	0.65 per cent
(b) " 3 grms. " ..	0.56 "	0.55 "
(c) " 10 " " ..	0.55 "	0.55 "

To determine further the nature of the residue, whether it was all silica, or wholly or partly a silicate, it was treated in the platinum crucible with a few drops of dilute sulphuric acid, and the crucible was nearly filled with a dilute solution of hydrofluoric acid. It was evaporated on the water-bath, and the excess of sulphuric acid removed with the free flame.

Residue in the Crucible obtained by Methods 1 and 2.

	Method 1.	Method 2.
(a) 1 grm. substance..	0.13 per cent	0.13 per cent
(b) 3 grms. " ..	0.12 "	0.12 "
(c) 10 " " ..	0.14 "	0.11 "

A blank test was made, using sulphuric and hydrofluoric acid in the crucible, and evaporated to dryness. No residue was obtained.

The residue in the crucible was determined and found to be:—

Aluminium and iron sulphate ..	0.08 per cent
Calcium sulphate.. ..	0.058 "
Magnesium sulphate	0.00 "
	0.138 "

Method 3.—To compare the insoluble residue obtained by fusion with alkaline carbonate with the amount obtained by the foregoing methods:—

A grm. of the fine rock powder was thoroughly mixed in the platinum crucible with 7 grms. of anhydrous sodium carbonate. The sodium carbonate used was a good quality of Merck's manufacture. It was further purified by dissolving a quantity in water and filtering. This after fractional crystallisation seemed to be entirely free from silica. The covered crucible was heated for fifteen minutes with a Bunsen flame, then with a blast-lamp to complete fusion. The cooled mass was transferred to a porcelain evaporating dish, and dissolved in dilute hydrochloric acid. Evaporation was continued on the water-bath until crystals began to appear. It was then stirred with a glass rod until a fine dry powder was obtained. It was treated with hydrochloric acid as in Method 2 before described. The insoluble residue obtained by this method amounted to 0.53 per cent. This treated with sulphuric and hydrofluoric acids left a residue of 0.16 per cent. The results are fairly concordant with those obtained by Methods 1 and 2, but on account of the difficulty of getting pure sodium carbonate and the length of time and the labour necessary to obtain the result, this process is not to be commended in rocks of this character. Indeed, Method 1 is greatly to be preferred whenever circumstances permit, on account of its simplicity and the shortness of the time required.

During the course of this work our attention was called to the estimation of silica as outlined by Treadwell in his excellent treatise on quantitative analysis (Treadwell-Hall, "Quantitative Analysis," p. 384). After removing the insoluble residue according to Method 2, it is stated that "as much as 5 per cent of the total amount (of silica) may

remain in the filtrate. In order to remove this, the filtrate from the first precipitate is once more evaporated to dryness on the water-bath, and kept on the water-bath for one or two hours or more." It is then filtered after treatment with hydrochloric acid and water in the usual manner. One grm., 5 grms., and 10 grms. of substance were used. In no case was even a trace of residue obtained by the second treatment. The experiment was varied by using a specimen of argillaceous limestone that contained 18 per cent of silica.

A second portion of residue could not be obtained from this specimen.

A complete analysis of the Bedford limestone resulted as follows :—

CaCO ₃	93.55 per cent
MgCO ₃	5.42 "
SiO ₂	0.55 "
Fe ₂ O ₃ and Al ₂ O ₃	0.50 "
	100.02 "

The condition of the iron was tested by placing 3 grms. of the powdered rock in a flask of 120 c.c. capacity, fitted with a bulb-tube and Bunsen valve. The material was dissolved in a small quantity of dilute hydrochloric acid. A few drops of the solution quickly withdrawn and placed on a porcelain tile in contact with a solution of potassium ferricyanide showed a slight tinge of blue. A few drops of a solution of potassium sulphocyanate were then quickly introduced into the flask, when a red colour was produced. The portion of the iron soluble in hydrochloric acid is therefore of both the ferrous and ferric forms. No attempt was made to determine each quantitatively on account of the small amount.

The writer acknowledges the assistance of Alys Boies Carson for making the experiments in this investigation.

Chemical Laboratory, Cornell College.
July 4, 1905.

ON THE OXIDATION OF PHOSPHORUS.

By W. P. JORISSEN.

1. In the discussion following the reading of the paper on "The Mechanics of Fire," by Prof. Armstrong, in the London Section of the Society of Chemical Industry (*Journ. Soc. Chem. Ind.*, May 15th, 1905), Dr. Brereton Baker made the following interesting statement :—

"He took three similar bits of glowing phosphorus, placed them in lead tubes, and over them a photographic plate in the dark. He wanted to measure the amount of light given out by these pieces of glowing phosphorus. One tube was charged positively from a large accumulator, another was charged negatively, and the third was left uncharged. The phosphorus was just moist enough to become a conductor. He left it about half-an-hour, and then developed the plates; under the positive tube he found a black mark; under the negative scarcely any; and the third was about the mean of the other two. That was only one experiment, and many more would be required to confirm the observations. It seemed to him this experiment, which of course required confirmation, might throw some light on the question as to whether ions were really produced, the positive ions of oxygen being attracted to one side, and the negative ions to the other. There were very few positive ions combining with the phosphorus; what became of them? They all knew that when phosphorus glowed ozone was produced. He did not measure the ozone coming from each piece of phosphorus, but if the hypotheses formed were correct, he would find little ozone at the positive phosphorus, whilst much would be produced at the negative."

This leads me to communicate that last year the following experiments were made by me (*Chem. Weekblad.*, 1904, i., 341):—Three photographic plates were wrapped in black paper in such a manner as to be wholly protected from the influence of the light. On each of them a very thin piece of mica was placed, and on this a small lump of phosphorus. They were covered by glass beakers, under two of which were put a very small dish with some ether and one with some turpentine-oil respectively.

In the dark it appeared that the phosphorus only glowed under the beaker, which did not contain any vapour of ether or turpentine-oil, as was to be expected.

After some seven hours it was only the plate exposed in this way to the action of the oxidising phosphorus that on developing was found to have been acted upon. An image of the mica film was seen on the darkened plate; but also an action had taken place under this film. The darkening ceased at the brim of the beaker.

These experiments were repeated after placing thin films of gold and silver over the plates. The result was the same; only on the place where two films had been put on top of each other, the darkening was somewhat less.

That Knoblauch had made an observation of the same kind was unknown to me at the time of my experiments. Some months ago I found in a paper of Bredig and Pemsel (*Arch. f. Wissensch. Photogr.*, 1899, i., 33), just then sent to me by the authors, the following communication:—"M. Knoblauch kindly informs us that phosphorus, like uranium, issues a photographic radium-like action which also penetrates through untransparent substances." It would be interesting to test also other spontaneously oxidising substances in this way. Frantz (*Zeit. f. Elektrochem.*, 1904, x., 593), who studied the luminous glow seen during several oxidation processes (Radziszewski, *Liebig's Ann.*, 1880, cciii., 305—336; Perkin, *Journ. Chem. Soc. Trans.*, 1882, xli., 363) and crystallisations, remarks:—"In more than one case, when during crystallisations and reactions a glow was observed, the rays were found to penetrate through black paper. Still a very prolonged exposure is necessary."

2. To these experiments I was led by the well-known observations about the ionisation of oxygen of the air in contact with phosphorus. In the first place, I mention the fact that the air, in which oxidation of phosphorus takes place, becomes a far better conductor for electricity than ordinary air, and that particles with opposite charges are to be found in the neighbourhood of oxidising phosphorus.* Traces of turpentine-oil, ether, and carbon disulphide, which among many other substances have the power of preventing (or delaying) the oxidation of phosphorus at a certain pressure of the oxygen (Joubert, *Thèses*, Paris, 1874, 43—45; Centnerszwer, *Zeit. f. Phys. Chem.*, 1898, xxvi., 3), remove this conductivity (Elster and Geitel, *Edgar Meyer and E. Müller, loc. cit.*).

In the second place, I mention the condensation of a steam jet in the presence of slowly oxidising phosphorus observed by R. von Helmholtz and Richarz.† Also when the luminous vapour is blown aside the action on the steam jet is not diminished. It is, however, not affected by ozone, hydrogen peroxide, or nitrous acid.

In the third place, I wish to draw attention to a very interesting observation made by van't Hoff (*Zeit. f. Phys.*

* See the papers mentioned by J. J. Thomson in his "Conduction of Electricity through Gases" 1903, 324; also Elster and Geitel, *Wied. Ann.*, 1890, xxix., 322; *Phys. Zeit.*, 1903, iv., 457; Harms, *Abhandl. der Radioaktivität und Elektrizität*, 1904, i., 293; Edgar Meyer and E. Müller, *Ber. Deutsch. Phys. Gesell.*, 1904, ii., 332; Bloch, *Thèses*, Paris, 1904, "Le Radium," August 15th, 1904.
† R. von Helmholtz and Richarz, *Wied. Ann.*, 1890, xl., 192; see also J. J. Thomson, *loc. cit.*, p. 334. Helmholtz and Richarz also observed an action of nitrogen oxide, ether, potassium, and sodium. In connection with my experiments on the activation of oxygen (*Zeit. f. Phys. Chem.*, 1897, xii., 34; 1897, xxiii., 667; *Arch. Néerl.*, 1897; see also J. W. Mellor, "Chemical Statics and Dynamics," 1904, 306). I also tried and found to act on the steam jet triethylphosphine, benzaldehyde, turpentine-oil, and a strong solution of sodium sulphide, all in the act of oxidation, their surfaces being enlarged by bringing some drops of them on a piece of blotting-paper (*Chem. Weekblad.*, 1904, i., 341).

Chem., 1895, xvi., 411). He shook a small quantity of phosphorus with a solution of indigo sulphonic acid and air, after having heated the vessel with the solution in water of 50° C. After violently shaking about thirty times, he put it in the water again. A kind of flame appeared and died away, only to reappear after repeated shaking.

About 9 m.grms. of phosphorus had not quite disappeared after the flame had returned 277 times. "According to the above mentioned flame phenomenon," he says, "something is present in the atmosphere of the vessel which prevents the phosphorus from oxidising; there is apparently enough oxygen left; there might be supposed to be a lack of phosphorus-vapour. On opening the vessel, however, the opposite is proved by the now appearing phosphorescence. On shaking with indigo, the hampering action, which I am inclined to ascribe to the electric charge, respectively to the positive or negative oxygen ions in excess, is annihilated, while sulphuric acid (perhaps on account of its conductivity) accelerates it in a high degree. And that the act of shaking, which enables the oxidation to take place again, is not to be attributed to saturating with phosphorus-vapour, is shown by the fact that without indigo, with phosphorus and water only, the whole of the typical flame phenomenon is not produced."

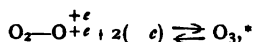
Speaking about the above named oxygen ions he says:—"If the pieces in question are charged positively and negatively, it may be easily understood that the substance, which is oxidised, prefers one of them, while the other gives an electric charge to the oxygen, which ends in the formation of ozone, the decolouration of indigo, &c."; and further, "the primary product formed in oxygen, which has been made active by phosphorus, is not ozone, for it prevents the phosphorescence of the phosphorus, while ozone favours this phenomenon" (Chappuis, *Bull. Soc. Chim. de Paris*, 1881, xxxv., 419).

3. R. von Helmholtz and Richarz concluded from their experiments, referred to above, that the action on the steam jet is caused by pairs of atoms, —O—O—, or by free atoms of oxygen.

The conclusion to which van't Hoff came has been already quoted.

Thirdly, as regards the ionisation of the oxygen during the oxidation of phosphorus and the kind of ions formed, I wish to refer to J. J. Thomson's "Conduction of Electricity through Gases," 1903, 324—325, to J. W. Mellor's "Chemical Statics and Dynamics," 1904, 309—312, and to the following papers:—E. Bloch, *Thèses*, Paris, 1904, "Le Radium," August 15th, 1904; F. Harms, *Fahrbuch der Radioaktivität und Elektronik*, 1904, i., 291).

Somewhat more extensively I wish here to treat of the reasoning of R. Schenck (*Sitz. Berichte Akad. Wissensch. Berlin*, January 7th, 1904). He remarks that without doubt during the oxidation of phosphorus electrons are formed, and that these transform oxygen into ozone. This formation of ozone, however, is not complete. He supposes an equilibrium to arise between oxygen, ozone, oxygen atom ions, and electrons, which may be represented by the symbol—



in which by O^{+e} an oxygen atom ion and by $-e$ an electron is meant.

He now supposes that the phosphorus or one of its products of oxidation (see Jungfleisch, *Comptes Rendus*, 1905, cxi., 444) becomes luminous under the influence of the ionised oxygen, and that the oxidation of the phosphorus takes place by means of oxygen atom ions.

"If now," he says, "we increase the pressure of the oxygen, the concentration of the ozone will become greater at the expense of the ions. If the concentration of the oxygen increases sufficiently, the number of the ions will at last grow smaller than the quantity which is required to

make the light perceptible to the eye. Hand in hand with this phenomenon goes the decrease of the reaction velocity according to the law of mass action."

Against this conclusion of Schenck the following may be argued:—

From the equilibrium supposed by him follows:—

$$\frac{C_{O_3} \cdot C_{O^{+e}} \cdot C_{-e}^2}{C_{O_2}} = k \dots \dots (1).$$

Now the concentration of the oxygen is very considerable in comparison with the other concentrations; thus we may write with some approximation:—

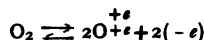
$$\frac{C_{O^{+e}} \cdot C_{-e}^2}{C_{O_2}} = k' \dots \dots (2).$$

Now, if the degree of ionisation decreases, the concentration of the ozone must become smaller and not greater as Schenck concludes.

The fact that phosphorus which does not glow, because the pressure of the oxygen is too high, becomes luminous if a trace of ozone is added, corresponds with formula (2) if we suppose that Schenck's hypothesis about the glowing of phosphorus by means of oxygen ions is a fact.

For, if the concentration of the ozone—which may be put as zero in oxygen in which phosphorus does not glow—is increased, the concentration of the ions will do the same. Now, according to Schenck's reasoning, the concentration of the ozone in the neighbourhood of the "boundary-pressure" of the oxygen would be considerable, which is not according to facts.

If, however, with van't Hoff we suppose the equilibrium



to exist,* then the degree of ionisation will become smaller on our increasing the pressure of the oxygen, without having to assume an increase of the ozone-concentration. The ionised oxygen will indeed have a larger volume than the ordinary oxygen.

But our views will remain incomplete if we cannot bring into account the influence of water vapour on the boundary-pressure of the oxygen. In this respect also a closer study of this pressure is important.

Helder, Holland, June, 1905.

City and Guilds of London Institute.—At a meeting of the Council held July 24th the diploma of "Associate of the City and Guilds Institute" was awarded to the following matriculated third-year students of the Central Technical College who have completed a full course of instruction as prescribed by the Council:—*Civil and Mechanical Engineering*.—C. J. Balding (Bramwell Medal), R. W. Allen, C. M. Baissac, A. M. Beale, G. E. W. Bridge, R. W. Buttemer, F. C. Cooper, J. A. Denney, L. J. M. Guggenheim, G. W. Halse, C. Herbert, J. Hodgkinson, C. B. Job, L. King, S. Lacy, A. J. H. Laing, A. R. Mitchell, J. E. Montgomery, K. Newton, A. R. Reed, L. M. Regnard, G. M. Smith. *Electrical Engineering*.—W. H. Grinstead (Siemens Medal and Premium), A. J. Aldridge, C. R. Bland, E. B. Brown, J. L. Cook, P. G. Dani, P. Eisler, R. R. Elliott, O. Faber, W. M. Hooton, H. R. Hudson, G. Johnson, N. H. Martin, C. R. McGowan, C. E. Nightingale, H. K. B. Reed, F. C. Street, F. W. Strickland, K. J. Thomson, F. L. N. Tuck, W. Turner, A. Vipan, E. C. Webber. *Chemistry*.—W. H. Eagle, F. J. Harris, W. J. Wilson.

In 1895, when van't Hoff (*Zeit. f. Phys. Chem.*, 1895, xvi., 411) supposed the equilibrium $O_2 \rightleftharpoons 2O$ to exist in oxygen, also if a spontaneously oxidising substance is absent, the hypothesis of the electrons had not been brought forward as it is now.

* Schenck uses another symbol which comes to the same thing; the above seems to me to be more evident.

THE HANDLING OF PRECIPITATES FOR
SOLUTION AND RE-PRECIPITATION.

By F. A. GOOCH.

IN many processes of analytical chemistry, the preparation of substances in pure condition is brought about by precipitation, solution, and re-precipitation; and sometimes this cycle of operations must be repeated. When a precipitate, gathered upon a filter, is easily acted upon by the appropriate solvent, the process of dissolving the precipitate from the filter is simple; but when the precipitate is refractory toward solvents or difficult to attack on account of its physical condition, as is the case with many gelatinous precipitates, the proper handling of the precipitate involves some inconvenience and delay.

In meeting such difficulties, I have found it advantageous to place within the ordinary paper filter, before filtering, a movable lining of platinum gauze, upon which the precipitate rests for the most part and with which it may be removed. The simplest form of this device is easily made by cutting platinum gauze to the shape shown in Fig. 1.



FIG. 1.

In ordinary use, this piece of gauze, folded to make a cone of angle a little less than 60° , and held by pincers at the point of overlapping, is placed within this filter and allowed to fit itself closely by the natural spring of the gauze when released.

Upon filters so prepared a precipitate may be collected and washed as usual; and, at the end of the operation, the cone with nearly all the precipitate may be transferred, by means of ivory-pointed pincers, to dish or beaker for suitable treatment. The small amounts of the precipitate which have passed through the gauze, being somewhat protected by the gauze against the compacting action of filtration and washing, are generally removable with ease from the filter by a jet of the washing-liquid. After washing, the gauze may be replaced within the same filter and serve for a second collection of the precipitate to be subsequently dissolved, in case double precipitation and solution are desirable. The final collection of the precipitate is, of course, made upon paper without the gauze lining, when precipitate and filter are to be ignited.

This device has proved very serviceable in the handling of such precipitates as ferric hydroxide, aluminium hydroxide, and basic acetate precipitations.

I have used also in the manipulations of such precipitates a regularly made cone of 60° , fitted with eyelets for handling; but the simple folded cone is, on the whole, more convenient.

Precipitates collected upon asbestos in the perforated crucible are frequently removable without difficulty by allowing a suitable solvent to percolate precipitate and felt; but in case the precipitate is pasty or compacted, solution in this manner may be unpleasantly slow. In such cases, it is convenient to remove the greater part of the precipitate, collected and washed in the usual manner, upon a disc of platinum foil, perforated, fitted with a wire handle, as shown in Fig. 2, and placed upon the asbestos felt before the transfer of the precipitate to the crucible. To make such a disc is the work of a few moments only; and by its use pasty precipitates, such as cuprous sulphocyanide

or the sulphides of the metals, are easily handled for solution.

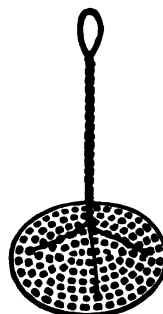


FIG. 2.

These simple devices so facilitate the manipulation of precipitates in many processes of analysis that they have seemed to be worthy of description.—*American Journal of Science*, xx., July, 1905.

THE ASSAYING OF TIN AND TERNE DROSSES.

By GEORGE P. MAURY.

THESE drosses are a heterogeneous mixture of the metal buttons from about 5 grms. in weight down to a size that will pass through about a forty mesh sieve, with oxides of tin, lead, iron, and zinc, zinc chloride, silica, alumina, partly burned carbonaceous matter, &c. It can readily be seen that a very large variation in results may occur unless special precautions are taken to put the sample in such shape that a correct average may be obtained in the portion taken for the assay.

The dross is received in two portions, together with the percentage of each in the car sample; the coarse, that did not pass through a twenty mesh sieve, and the fine, that did pass through a twenty mesh sieve in sampling.

The relative amounts of fine and coarse vary widely, running from 0.25 per cent coarse to 0.20 per cent coarse, depending upon the richness and physical condition of the dross.

The conditions naturally divide the method of analysis into, and we shall consider it under three heads:—"The Preparation of the Sample," "The Assay," and "The Analysis of the Button from the Assay."

Preparation of the Sample.

Under this head I will describe two methods, either of which gives good results:—

Method by oxidation.

Method of separating the coarse from the fine, and weighing each portion.

Method of separating the coarse from the fine.

For convenience we will call the original coarse sample A and the original fine sample B; for example, we take a dross containing 10 per cent coarse, which we call A, and 90 per cent fine, which we call B.

All of A is taken, in this case 200 grms., ground until everything will go through a one hundred mesh sieve, except the metal beads or buttons; these are flattened out—the object in so doing is to be sure that all the small pieces of brick, gravel, &c., are broken up, and to know that nothing of the kind is left with the buttons of metal; after this operation there are (see calculation) 50 grms. of fine, equal to 25 per cent, and 100 grms. of coarse, equal to 75 per cent.

For a 300 grm. sample, there would be 10 per cent of 300 grms., or 30 grms. of A, and 90 per cent B, which is equal to 270 grms.

The 270 grms. are ground until everything except the metallic buttons will pass a one hundred mesh sieve, the buttons are flattened as described above under the coarse. Upon weighing the coarse and the fine, the coarse from B equals 30 grms., which is 11.11 per cent, and the fine equals 240 grms. or 88.89 per cent. The coarse from A was 75 per cent, and there would be required for a 300 grm. sample 30 grms. of A; then 75 per cent of 30 grms. equals 22.50 grms. from A, and 11.11 per cent of B equals 30 grms. of coarse, or a total of 52.50 grms., equalling 17.50 per cent of coarse.

These amounts are weighed out and mixed.

For the fine we had 25 per cent of B or 25 per cent of 30 grms., equal to 7.50 grms. Of the fine in B there was 88.89 per cent of 270 grms., equal to 240 grms.; a total of 247.50 grms., equal to 82.50 per cent of 300 grms., the amount of the sample taken. These are thoroughly mixed.

Then the assay sample will consist of 17.50 per cent coarse and 82.50 fine. On a 20 grm. assay this would be 3.50 grms. of coarse and 16.50 grms. of fine.

Calculation.

10 per cent coarse A	300-grm. sample	30 grms. of A
90 per cent fine B..	equals	270 " " B
A yields	Fine.. 50 grms. equals	25 per cent
	Coarse 150 " "	75 " "
B yields	Fine.. 240 " "	88.89 " "
	Coarse 30 " "	11.11 " "

New sample:—

Coarse	10 per cent of A equals 30 grms.,	75
	per cent of which is coarse equal to	22.50 grms.
	90 per cent of B equals 270 grms.,	
	11.11 per cent of which is coarse	
	equal to	30.00 "
	Total coarse equals 17.50 per cent	52.50 "
Fine	A 10 per cent of 300 equals 30 grms.,	
	25 per cent of which is fine equal to	7.50 "
	B 90 per cent of 300 equals 270	
	grms., 88.89 per cent of which is	
	fine equal to	240.00 "
	Total fine equals 82.50 per cent	247.50 "

Assay | Coarse = 17.50 % for 20 grm. | 3.50 grms. coarse
sample | Fine = 82.50 % sample .. | 16.50 " fine

Oxidation Method.—About 400 grms. of the sample accurately weighed are taken, placed in a large evaporating dish (12 in. in diameter) moistened with water, and nitric acid added very cautiously at first, then heat gently until solution is complete. It usually takes about as many c.c. of nitric acid to oxidise sample as grms. of sample taken (this may vary, of course, as the dross is rich or lean in metallic particles). Add cautiously enough sulphuric acid to replace nitric acid left (usually about one-third to one-fourth of amount of nitric used), evaporate to dryness, and heat to drive out nitrates and as much sulphuric acid as possible, break up mass, and grind to pass a 100 mesh sieve, then heat to a red heat for at least one hour to decompose all sulphates (to prevent trouble from boiling over the top of the crucible, also to reduce amount of potassium cyanide required in assay), allow sample to cool, and weigh accurately; sample will weigh more on account of oxygen taken up.

We find it weighs 504 grms., which divided by 400 (amount of the sample taken) equals 1.26, which is the factor by which to multiply the result obtained in assaying; that is, if the sample shows 30 per cent of the metal by assay, this multiplied by 1.26 equals 37.80 per cent the amount in the original dross.

The Assay.—Take 20 grms. of the sample and 100 grms. of potassium cyanide in a "G" or "J" crucible, mix the sample with about 50 grms. of the ground cyanide, and place about 40 grms. of the balance in the bottom of the

crucible, then add the sample mixed with the cyanide, settle well by tapping, and add the balance of the cyanide, spreading it in a thin layer over the top of the sample.

A blacksmith's forge is used to reduce the assay, and it is very satisfactory. While authorities on assaying tell you to use a bright red or white heat, our best results have been obtained above a white heat, in fact as high as an air blast and a coke fire will give in a forge just short of melting a Denver crucible.

High temperatures have given the highest results and low temperatures invariably give low results. The crucible is allowed to stay in the furnace from five to ten minutes after fusion begins. The high iron content in the dross and the button raises the fusion point of the button, and makes the high temperature necessary for a correct assay. The crucible is allowed to cool, and is broken, the button is thoroughly cleaned, boiled in water, dried, and broken up by hammering, and is washed again in boiling water, dried, and weighed as a check on the direct determinations of the contents of the button.

Analysis of the Button.—After weighing the button it is dissolved in hydrochloric acid with a small amount of nitric acid, diluted to 1 litre, and 50 c.c. or one-twentieth of the solution taken for the determination of iron by titration with potassium bichromate.

Fifty c.c. is taken for the determination of tin, copper, zinc, and lead; this is made nearly neutral, 30 c.c. of ammonium sulphide solution added, and digested for about thirty minutes. Hydrogen sulphide is passed through the solution, and the solution filtered. The iron, lead, copper, and zinc are dissolved off the paper with strong hydrochloric acid and a few drops of nitric acid, boiled, and brought nearly to neutral point with ammonia; 30 c.c. more ammonium sulphide added, and digested as before. Usually three ammonium sulphide separations are necessary to separate the tin from the other metals.

The iron, lead, &c., are then dissolved as before, sulphuric acid added, and evaporated until fumes of sulphuric anhydride are given off, for lead by the sulphate method. Make double hydrate of filtrate for zinc, and determine by hydrogen sulphide and sodium carbonate.

The precipitate of iron is next dissolved and tested with hydrogen sulphide to see if any tin has gone through with the iron.

The filtrates from the ammonium sulphide digestions are combined and made slightly acid with sulphuric acid to precipitate the tin as a sulphide; it is filtered, thoroughly washed with hot water, burned, and weighed.

Extreme care is exercised to prevent volatilisation of tin as proto-sulphide. Ammonium carbonate is added to remove the last of the sulphuric anhydride.

When percentage of iron is high in an alloy of tin and iron, the separation of tin by oxidation with nitric acid is unsatisfactory, as part of the iron will be carried down with the oxide of tin, and some of the tin will go in solution with the nitrate of iron.

Separation of tin and iron by hydrogen sulphide in acid solution gave very unsatisfactory results; if the solution is acid enough to hold up the iron, some of the tin will be held in solution, and if all the tin precipitates some iron will be carried down with it.

The separation with sodium sulphide proved unsatisfactory on account of trouble in washing out sodium salts.—*Proceedings of Engineers' Society of Western Pennsylvania*, xxi., No. 2.

Chromic Sulphate.—Albert Colson.—The solution of a metallic oxide in an acid diluted with water by definition gives a dissolved salt. This is neutral, acid, or basic, according to the proportion of the reacting substances, and should preserve the essential chemical properties of the species of salt obtained. The author now shows that the solution of chromic oxide in dilute cold sulphuric acid gives a variety of sulphate in which the sulphuric acid resists all reagents.—*Comptes Rendus*, cxli., No. 2.

ELECTROLYTIC OXIDATION OF
HYDROCARBONS OF THE BENZENE SERIES.*

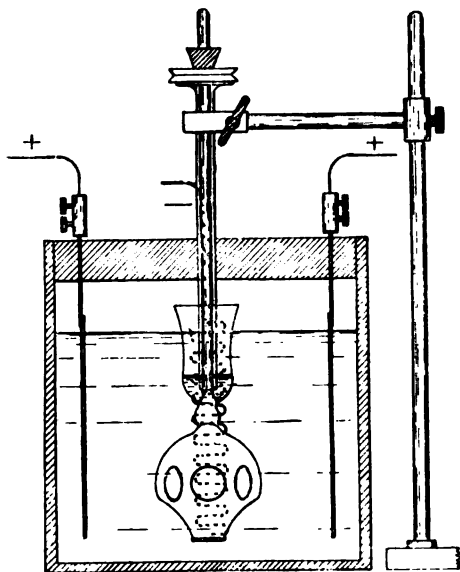
PART II. ETHYLBENZENE, CUMENE, AND CYMENE.

By H. D. LAW, and F. MOLLWO PERKIN.

INTRODUCTION.

IN continuation of the work upon the electrolytic oxidation of the hydrocarbons of the benzene series, we have now studied the oxidation of hydrocarbons containing groups other than methyl, or compounds which contain the methyl group and another group, as for example cymene, in which there is a methyl and isopropyl group in the same nucleus.

In our first communication upon the oxidation of substances containing the methyl group (*Trans. Faraday Soc.*, Jan., 1905, i., p. 31) it was shown that in all cases the methyl group was oxidised mainly to the aldehyde, or second stage of oxidation, and where there was more than one methyl group in the nucleus that chiefly the mono-aldehyde was produced, and attention was drawn to the comparative stability of the aldehyde group to electrolytic oxidation, because in no case was the corresponding acid obtained. A small quantity of a substance, which did not react with sodium bisulphite, and was, therefore, not an aldehyde, was also obtained. This substance we have since proved to be the corresponding alcohol.



In the present instance, as is the case with toluene, the xylenes, and mesitylenes, the most satisfactory method of oxidation has been to dissolve the hydrocarbon in an excess of acetone, and add the mixture to the electrolyte, the bulk of which was usually rather less than the bulk of the acetone added. For example, a good mixture is 300 to 400 c.c. of acetone and 200 c.c. of 5 to 10 per cent sulphuric acid.

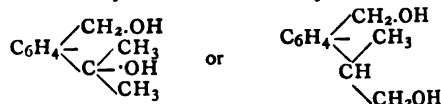
In the paper just referred to (*loc. cit.*) we drew attention to the difficulty experienced owing to the continual increase in concentration of the anode solution by the transference of the SO_4^{--} ions to this compartment when the electric current was passed. As for 50 grms. of hydrocarbon about 70 ampere hours of current are required to be used, it follows that towards the end of the operation the sulphuric acid concentration becomes very considerable. We were of the opinion that this high concentration and the fact that an aldehyde and acetone were present, would probably

tend to cause condensation and increase the quantity of unworkable tarry product always obtained in greater or less quantities. In a paper shortly to be published, it will be shown that by working without a diaphragm in the case of toluene, it has been found possible to increase the yield of benzaldehyde obtained from about 8 per cent to 18 or 20 per cent. The apparatus which was employed and found satisfactory is shown in the accompanying illustration. It consists of a circular glass vessel capable of holding about 750 c.c. The jar is closed by means of a large cork, through the centre of which passes a glass stirrer. Two anodes of sheet platinum, having together a total surface of 1.5 sq. d.cm., are placed at opposite sides of the vessel, and in between them and opposite to each other, two cathodes of stout platinum wire, which have the form of loose spirals. The total area of the cathodes was usually about 20–25 sq. c.m. By employing this large anode surface and small cathode surface, the oxidation is very complete and the reduction is practically nil. The amount of alcohol found is about the same as when a porous cell is used; therefore, the alcohol is an oxidation product and is not formed by the reduction of the aldehyde. We have also reduced the strength of the sulphuric acid employed as the electrolyte from about 10 to 5 per cent. As in the previous case when dealing with hydrocarbons containing the methyl group, we have invariably obtained an aldehyde and also an alcohol, but the oxidation has never gone so far as to produce the corresponding acid.

With ethyl benzene, the secondary alcohol $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ was obtained in considerable quantity, and also a small quantity of what was probably the primary alcohol $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$, but this was not obtained in a state of sufficient purity to give good analytical numbers. Benzaldehyde was also obtained, but only after the bulk of the hydrocarbon had been converted into the alcohol. It is interesting to compare this oxidation with the products obtained by purely chemical methods.

When oxidised with chromic and sulphuric acids, or with nitric acid, ethyl benzene yields benzoic acid. But on oxidation with chromic acid, dissolved in acetic acid, acetophenone is said to be produced. It might have been supposed that in our case, on further oxidation, the secondary alcohol would have yielded acetophenone, but we were unable to find any.

Cymene (*p*-methylisopropylbenzene) yielded about 20 per cent of a mixture of alcohols and about 10 per cent of an aldehyde. On analysis, the alcohol boiling-point $235\text{--}240^\circ$, which occurred in the largest proportion, was found to be a dihydric-alcohol, and may be either—



The lower fraction $215\text{--}220^\circ$ is a mixture of a mono- and a dihydric-alcohol.

The aldehyde obtained is $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CHO} \\ \diagdown \text{C}_3\text{H}_7 \end{array}$, showing that the methyl group is more readily attacked than the isopropyl group. When cymene is oxidised with potassium permanganate hydroxyisopropylbenzoic acid, $\text{OH}\cdot\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\cdot\text{COOH}$, is produced, which on further oxidation is converted into terephthalic acid. Cold nitric acid yields *p*-methyl tolyl ketone, but the hot acid gives *p*-toluic acid, in this last case the isopropyl group being attacked before the methyl. Cumene (isopropylbenzene), on oxidation with chromic acid, gives benzoic acid. But with chromyl chloride acetophenone and hydratropaldehyde we find that electrolytic oxidation yields an aldehyde, boiling-point $220\text{--}225^\circ$, and a small quantity of a di- and monohydric-alcohol. On one occasion benzaldehyde was obtained. Owing to the cumene which we had not being pure and apparently consisting of a mixture of cumene and other hydrocarbons, the results obtained were not so satis-

* Read before the Faraday Society, July 3, 1905.

factory as we would have liked. We hope, therefore, on a future occasion to examine this substance further.

EXPERIMENTAL.

Ethylbenzene.

The ethylbenzene which we employed was prepared synthetically by the action of sodium upon a mixture of bromobenzene and ethyl iodide.

Two quantities of 50 grms. each were subjected to oxidation. The ethylbenzene was dissolved in 400 c.c. of acetone, and added to 200 c.c. of 10 per cent sulphuric acid and placed in the electrolysis vessel just described. The whole apparatus was placed in a vessel through which cold water was caused to circulate. Before commencing the electrolysis the mixture was brought into an homogeneous emulsion by means of the stirrer, and the stirring continued during the whole operation.

Anode surface	150 sq. c.m.
Cathode surface	25 sq. c.m.
Current	2 ampères.
E.M.F.	5—6 volts.
Temperature	18°

The anode C.D. was therefore 1.3 ampères per sq. d.cm. of surface.

The current was passed for 40 hours, so that 80 ampère hours of current was employed. This is about one-third less than the theoretical amount of current required according to Equation IV. (*prox.*) to convert the whole of the hydrocarbon into benzaldehyde. The acetone was now distilled off and the dark oily product subjected to steam distillation. The light yellow oily distillate was separated from the aqueous layer, which was then extracted with ether. The ethereal solution was mixed with the oil, and then an excess of a saturated solution of sodium bisulphite added. After standing for 24 hours the bisulphite compound was filtered off. On decomposing this a small quantity of an aldehyde, which boiled at 180°, was obtained. This is the boiling-point of benzaldehyde, and its identity was further proved by exposing it to the air when it became oxidised to benzoic acid m.p. 119°. The yield of benzaldehyde was 3 grms., that is 6 per cent.

The ethereal solution obtained after filtering off the bisulphite compound was washed with water and sodium carbonate and dried over anhydrous sodium sulphate. The ether was distilled off, and on distilling the following fractions were obtained:—

I. 100—170° 8 grms.	} from 100 grms. of ethylbenzene.
II. 170—206° 16 grms.	
III. 206—220° 2 grms.	
Residue about 1 grm.	

The lowest fraction was mainly unchanged ethylbenzene and was not further examined. Fraction II., which on re-distillation almost all passed over between 200—202°, was analysed.

Substance = 0.1130, $H_2CO_2 = 0.3240$, $H_2O = 0.0804$:—

Found.	Calculated for $C_8H_{10}O$.
C = 78.21	C = 78.68
H = 7.91	H = 8.20

These numbers and the boiling-point show the substance to be the secondary alcohol phenyl methyl carbinol, $C_6H_5.CH(OH)CH_3$, the boiling-point of which is given in the literature as 202—204°.

There was only a very small quantity of the higher fraction No. III. after re-fractionation which boiled at 210°, and this, therefore, was not analysed. Its boiling-point, however, shows it to be the primary alcohol phenyl ethyl alcohol, $C_6H_5.CH_2.CH_2.OH$, whose boiling-point is 212°, the same as found by us.

In a second oxidation no aldehyde was obtained, only the alcohols being produced. In this case there was also a

small quantity of unchanged ethyl benzene, the oxidation having been interrupted before the whole of it had been attacked. There was always a very considerable quantity of tarry products obtained.

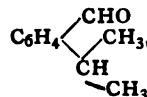
Cymene.

The oxidation of this product was carried out in exactly the same manner as that of the ethyl benzene. The current conditions being:—

Anode surface, 150 sq. c.m.
Cathode surface, 20 sq. c.m.
Current density at anode, 1.25 ampères per sq. d.cm.
E.M.F.

In all 200 grms. of cymene was subjected to oxidation, 50 grms. being oxidised in each experiment. The products of oxidation were worked up together. The excess of acid was neutralised with sodium carbonate and the acetone distilled off, the residue being subjected to steam distillation. The distillate after shaking out with ether was then treated with sodium bisulphite. In order that the whole of the aldehyde should be converted into the bisulphite compound, it was found advisable to allow the mixture to stand in contact with the sodium bisulphite for at least a week.

The bisulphite compound was filtered off, decomposed with sodium carbonate, and the aldehyde steam distilled; the distillate extracted with ether, which after drying with calcium chloride was distilled off and the fragrant-smelling aldehyde distilled. It almost all passed over at 235—237°. This shows it to be cumene aldehyde—



the boiling-point of which is 236.5°. It therefore follows that the oxidation as far as aldehyde formation is concerned only took place in the methyl group. In order to further prove that this substance is cuminaldehyde, a small quantity was exposed to the air for some days. By this means it was converted into the acid which, after re-crystallising from acetone and acetic acid, melted at 116°, showing it to be cumic acid, the melting point of which is given as 116° in the literature.

Carbasone.

This substance, which has not previously been prepared, was made in the usual manner. It is moderately soluble in absolute alcohol, from which it crystallised in shining pearly plates, m. p. 206—208°, with decomposition. A nitrogen determination was made, when the following numbers were obtained:—

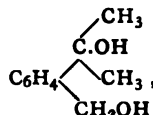
Substance 0.1046, Bar. = 754 m.m., $t = 24^\circ$, $N = 19.6$ c.c.

Found.	Calculated for $C_{11}H_{15}N_2O$.
N = 20.84	= 20.49

The portion which did not react with sodium bisulphite, and which consisted of 40 grms., was distilled, when the following fractions were obtained: I. 200—240°, II. 240—280°.

On refractionation two fractions were obtained: I. 210—215°, II. 222—224°.

The analysis of the higher fraction showed it to consist of a di-alcohol, probably—



but as these di-alcohols do not appear to be known, we are at present unable to decide which it is.

Substance = 0.1360, CO₂ = 0.3580, H₂O = 0.1010.

Found.

Calculated for C₁₀H₁₄O₂.

C = 71.79

C = 72.29

H = 8.25

H = 8.42

It was not found possible to obtain satisfactory numbers for the lower fraction, but it undoubtedly consists of a mixture of the mono- and di-alcohols, as the following numbers show :—

Substance = 0.1070, CO₂ = 0.3016, H₂O = 0.0880.

Found.

Calculated for C₁₀H₁₄O.

C = 76.87

C = 80.00

H = 9.13

H = 9.33

Cumene.

There was considerable difficulty in obtaining pure cumene. The product we finally used was obtained from Kahlbaum, and it boiled at 160–170°. This was repeatedly shaken out with small quantities of strong sulphuric acid until the acid ceased to be coloured. On steam distillation and subsequent fractionation it all passed over between 155° and 158°. Pure cumene, according to the literature, should boil at 153°. The results of our work show, however, that the bulk of this product did actually consist of cumene. 150 grms. of the cumene thus purified were mixed with 350 c.c. acetone and 200 c.c. of 5 per cent sulphuric acid and electrolysed for forty-eight hours. This is equivalent to 120 ampère hours, whereas theoretically 90 ampère hours are required to convert one of the methyl groups into an aldehyde.

Current = 2.5 ampères.

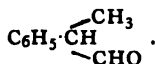
C.D. = 1.66 ampères per sq. d.cm.

E.M.F. = 2.5–4 volts.

Temperature = 18–20°.

At the end of the time the acetone was distilled off, and the dark brown oily residue steam distilled. The distillate was extracted with ether, and treated with sodium bisulphite. At the end of twelve hours scarcely any bisulphite compound had formed, so it was allowed to stand altogether for a week, when a considerable amount had formed (8 grms. of dry product, corresponding to 4.5 grms. of aldehyde). The amount of unchanged cumene recovered was 75 grms. and about 4 grms. of an alcohol substance, the rest of the cumene having been converted into a resinous substance. The large amount of cumene recovered and the small amount of oxidation products obtained show that the isopropyl group is not all readily attacked by electrolytic oxidation.

The aldehyde obtained from the bisulphite compound was fractionated. In the first place two fractions boiling at 200–220° and 220–225° were obtained. On refractionation less than 1 grm. came over below 220°, the rest boiling between 220° and 225°. Analysis showed that the aldehyde was evidently a mixture of cuminaldehyde and hydiatrop-aldehyde—



The remainder of the aldehyde was therefore dissolved in alcohol, and treated with semicarbazine hydrochloride and sodium acetate, whereby it was converted into a carbazone. The carbazone was found to consist of two substances, one of which was only soluble in absolute alcohol with difficulty, but the other was fairly soluble. Owing to their different solubilities a separation was effected by crystallisation from absolute alcohol. The portion which dissolved with difficulty separated out in the form of fine sandy crystals. The melting-point was not very definite, as after three crystallisations the substance melted at between 216° and 221°. The other substance was evidently the carbazone of cumenic aldehyde, but it was not obtained quite pure, and melted at 194–202° (the carbazone of cumenic aldehyde melts at 206–208°).

A nitrogen analysis gave the following numbers :—

Substance = 0.1613, Bar. = 758, *t* = 28, N = 32.5 c.c.

Found.

Theory for C₁₀H₁₂N₄O.

N = 22.06

N = 21.99

On one occasion, when the amount of current passed was considerably more than that theoretically necessary, a mixture of this aldehyde and benzaldehyde was obtained, the presence of benzaldehyde being proved by obtaining benzoic acid.

The alcoholic portions from several experiments, amounting in all to about 7 grms., were carefully distilled, when fractions boiling at 215–220° and 235–240° were obtained. Owing to the small quantity we had to deal with, it was not possible to refractionate our products. They were therefore analysed separately, and although good analytical numbers could hardly be expected, the numbers obtained showed that the lower fraction was a practically pure monohydric-alcohol and the higher fraction a mixture of the dihydric-alcohol and monohydric-alcohol.

Analysis of lower fraction 215–220° :—

Substance = 0.110, CO₂ = 0.3190, H₂O = 0.0855.

Found.

Calculated for C₉H₁₀O.

C = 79.09

C = 79.41

H = 8.63

H = 8.82

Analysis of higher fraction 235–240° :—

Substance = 0.1100, CO₂ = 0.3070, H₂O = 0.0776.

Found.

Calculated for C₉H₁₀O₂.

C = 76.12

C = 71.05

H = 7.84

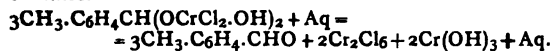
H = 7.95

As these alcohols do not appear to be known, we are unable to say whether the monohydric-alcohol obtained by us was the primary or tertiary alcohol. In all probability, however, as we have obtained an aldehyde, the alcohol is the primary alcohol, and the dihydric-alcohol is probably the dihydric-primary alcohol.

DISCUSSION OF RESULTS.

In connection with the electrolytic oxidation of substituted hydrocarbons of the benzene series, several very interesting facts have been brought out. The oxidation in acid solution is much less violent than is usually supposed, and certain groups which are extremely readily attacked by even the mildest of ordinary oxidising agents, such as the aldehyde group, are relatively stable when acted upon electrolytically. Thus when oxidising toluene or the xylenes, it was found that the methyl group was oxidised to the alcohol and then to the aldehyde, but that so long as there was any unchanged hydrocarbon present the aldehyde group was apparently unacted upon. Furthermore, that in the case of the xylenes one CH₃ group was invariably attacked before the other, and that until practically the whole of the xylene had been converted into the monohydric-alcohol, or aldehyde, the second CH₃ group was not attacked; the same is the case with the mesitylenes. The cause of this is probably to be traced to the protective action of the —CH₂OH or —CHO groups, both of which are more negative in character than the original —CH₃ group. The protective action of a negative group is strikingly shown when it is endeavoured to oxidise the cresols or the nitro-toluenes, the oxidation of these substances being extremely difficult, especially by electrolytic means. This characteristic has also been brought out in the oxidation of cumene, where the aldehyde C₃H₇.C₆H₄.CHO is the main product, the methyl group being first attacked and preventing further action upon the isopropyl group. In isopropyl the hydrogen atom in the tertiary position is usually considered the most readily attacked by oxidising agents. But to judge from the results obtained on oxidising cumene and cumene, the hydrogen atoms in the methyl group are more readily attacked when electrolytic methods of oxidation are employed.

In what manner, then, does electrolytic oxidation take place? When hydrocarbons are oxidised by chemical methods, the alcohol is rarely produced,* and the aldehyde only when CrO_2Cl_2 is employed as oxidising agent. In this latter case, the first action is the formation of an unstable combination between the chromyl chloride and one of the methyl groups of the xylene. For example, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3 + 2\text{O}_2\text{CrCl}_2 = \text{C}_6\text{H}_3(\text{CH}_2\text{CH}(\text{O}(\text{CrCl}_2\cdot\text{OH}))_2$. This is then decomposed by water with formation of the aldehyde, so that we may consider this a case of hydrolytic oxidation.



From our results it appears that in electrolytic oxidation, carried out in dilute acid or alkaline solutions, the hydroxyl group is the oxidising agent, and not oxygen.

In solutions containing sulphuric acid or other substances, such as potassium sulphate, there are beside SO_4 ions also OH' ions.

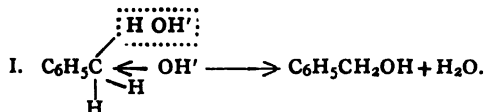
But according to the law of mass action, the product of the concentrations of the hydrogen and hydroxyl ions is always constant, and is independent of the other substances which may be present. Now the transport velocity of the OH' ions is far greater than that of the SO_4 ions, therefore there will be a tendency for them to group round the anode; they will therefore rather be discharged than the SO_4 ions.

According to Le Blanc, in the electrolysis of water a primary decomposition takes place. The actual electrolysis—i.e., the conductivity—is brought about by all the ions in the solution, but at the electrode that action takes place which proceeds most easily; this is the separation of the hydroxyl and hydrogen ions. We consider that the results of our work bear out Le Blanc's assumption that, provided the current is not too strong, the electrolysis of water is a primary reaction. We have worked throughout with fairly low currents, never exceeding and rarely reaching a greater density than 1.5 ampères per square decimetre of anode surface.

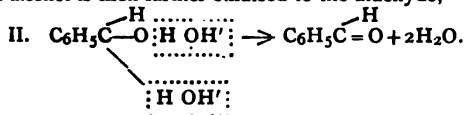
Where it is desired to form products by the action or union of ions other than hydroxyl, it is always necessary to have high concentration of the solute, and equally important to employ a high current density at the anode. Thus, in the formation of persulphuric acid or of chlorates or hypochlorites, strong solutions and very high current densities are always found necessary.

The current employed by us was too high for the reaction to be entirely primary, and this probably accounts for the fact that considerably more than the theoretical amount of current was required to complete the oxidation. Furthermore, we are not prepared to say that no part of the oxidation is due to oxygen liberated at the anode.

Assuming the oxidations to be produced by the action of the hydroxyl group, the following equations will explain the reactions which take place. With toluene and the xylenes the primary alcohol is first formed thus:—



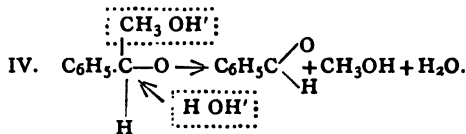
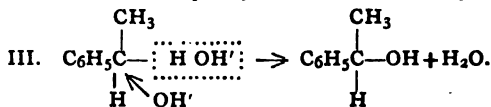
The alcohol is then further oxidised to the aldehyde,—



With ethylbenzene it is mainly the hydrogen attached to the β -position which is attacked, therefore no aldehyde is

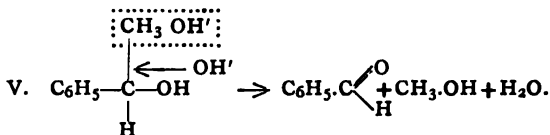
* When cymene is oxidised with potassium permanganate, $\text{OH}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{COOH})$ is produced (*Ber.*, xiv., 484). In this case the alcohol is produced owing to the hydrogen atom in the tertiary position being attacked, a tertiary alcohol being the only possible product.

obtained; further oxidation could only produce acetophenone, which, however, we have not obtained, although a portion has been completely oxidised to benzaldehyde.



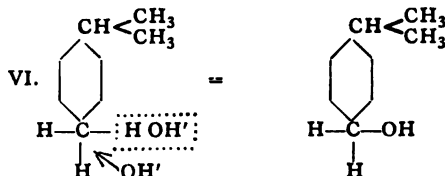
We have not found methyl alcohol in our solutions, and supposing it is produced it would be a very difficult matter to show its presence in a mixture containing such a large amount of acetone as was employed to dissolve the ethylbenzene. If, however, one OH' unites with the H of the alcoholic group, the oxygen would now unite with the carbon by a double bond, and the CH_3 would be forced off, and might at the same time unite with an hydroxyl.

Or this, by supposing the OH' ion on discharge to unite with the CH_3 group, which then being overloaded breaks off, and another hydroxyl group takes its place. We now



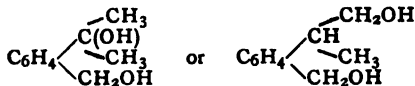
have two hydroxyls attached to one atom, and, as is well known, the tendency is under such conditions for water to be split off, with the result that an aldehyde is produced. The same explanation may be used to explain the aldehyde formation in II. and VIII.

Turning to cymene, we have a comparatively simple case, the first group acted upon being the methyl group. For this the Equation I. for toluene applies:—



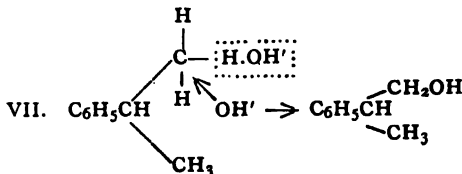
This is then further oxidised to cuminaldehyde, for which we need not write the equation.

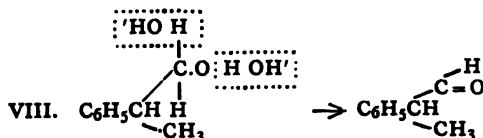
We are not able at present to say whether the dihydric-alcohol obtained by us is—



The fact of cumene forming the primary alcohol, which is proved by the formation of an aldehyde, goes to show that in all probability the dihydric-alcohol in the case of cumene is the dihydric-primary alcohol. This is a matter which we hope to clear up on subsequent investigation.

In the case of cumene the main reaction appears to be—





The dihydric-alcohol being formed by a similar oxidation of the second methyl group. Or it may be by oxidation of the tertiary hydrogen atom.

With reference to cumene, a little consideration shows that it is not a matter for surprise that the isopropyl group is not readily attacked. Genvresse (*Bull. Soc. Chim.*, 1893, [3], ix., 219) has shown that when normal propylbenzene is acted upon by chlorine at boiling temperature, the halogen enters the side chain. When, however, isopropylbenzene is treated in the same manner, the chlorine enters the nucleus. We hope to be shortly in a position to try further experiments with both normal propyl and isopropylbenzene.

Renard (*Comptes Rendus*, xci., 175) states that on electrolysis a mixture of benzene, sulphuric acid, and alcohol, he obtained phenose, $\text{C}_6\text{H}_6(\text{OH})_6$. Although several attempts have been made in this laboratory to prepare phenose by this means, we have not so far been successful. The assumption of hydroxylic oxidation makes it quite probable that such a substance might be obtained by oxidising benzene electrolytically. It should be quite possible, given the right conditions, to add two, four, or six hydroxyl groups to benzene. But considering the impossibility of obtaining hexahydrobenzene by actual reduction of benzene, it is not probable that the reaction would be an easy one to carry out.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 2, July 10, 1905.

Comparison of Properties of various Steels.—Léon Guillet.—The author's researches on certain steels which are alloys of iron, carbon, and a third substance show that a micrographical observation of such steels lead to an extremely interesting conclusion, both from the point of view of the commercial use of the steels, and even of their composition. The single case of perlitic steel still remains doubtful.

Hydrated Ferric Sulphate: Molecular Transformations.—A. Recoura.—The author finds that when a solution of ferric sulphate is left to evaporate, the solidification takes place in two phases. When the liquor has acquired a sufficient concentration the basic sulphate, $6[\text{Fe}_2\text{O}_3, 3\text{SO}_3] \cdot \text{Fe}_2\text{O}_3$, separates out, after which the acid liquid combines with the basic sulphate, and a yellow solid product is obtained of composition $\text{Fe}_2\text{O}_3, 3\text{SO}_3, 9\text{H}_2\text{O}$. The yellow sulphate behaves as a very unstable compound of the basic and acid sulphates. The white sulphate is much more stable.

A Dextro-dilactide.—E. Jungfleisch.—The author's investigations on dilactides show that the dilactide (*d* 1) is only formed after prolonged action of heat, the *d*-lactic acid changing very gradually into the inactive derivative by compensation, and so conforming to the general rule. By reducing to a minimum the time of distillation, it is possible to obtain the *d*-dilactide. This substance gives on analysis and cryoscopic examination results showing it to have the formula $\text{C}_6\text{H}_8\text{O}_4$.

Hydrogenation of Ketoximes. Synthesis of New Amines.—A. Mailhe.—By direct hydrogenation of the

oximes by the use of finely-divided metals, such as nickel and copper, the primary and secondary amines are formed with good yield. The formation of the secondary amines proves the reduction of the ketoximes—that is to say, those compounds in which the remaining NH is united to a secondary term, CH—substances generally very difficult to prepare. Except for di-isopropylamine, they were hitherto altogether unknown, but by the present method of direct hydrogenation of the ketoximes in presence of finely-divided nickel and copper they are easily prepared.

Synthesis of a New Leucine.—L. Bouveault and René Locquin.—The authors obtain the best results by the hydrogenation of their oximide ether by means of sodium in cold alcoholic solution, the neutrality of the solution being maintained by continual additions of alcohol saturated with hydrochloric acid gas. They thus prepare, with a yield of about 60 per cent, α -amino-butyl acetate of ethyl—the ethylic ether of the required leucine. It is a colourless liquid with a disagreeable smell, boiling at $90-92^\circ$ under a pressure of 15 m.m.

Sparteïn: Symmetric Character of the Molecule.—Charles Moureu and Amand Valeur.—The authors perform a series of experiments on sparteïn to prove that the positions occupied by the two atoms of nitrogen are symmetrical with regard to one another.

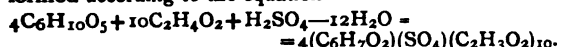
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 8, 1905.

Synthesis of Hydrazoic Acid.—Arthur Wesley Browne.—The author has synthesised hydrazoic acid by dissolving hydrazine sulphate in water, adding sulphuric acid and hydrogen peroxide, and heating to a moderately high temperature in a distilling flask. It was found that the presence of a considerable excess of hydrogen peroxide reduced the yield, while more hydrazoic acid was formed as the amount of sulphuric acid present in the solution was increased up to a certain limit. The equation $3\text{N}_2\text{H}_4 + 5\text{H}_2\text{O}_2 = 2\text{HN}_3 + 10\text{H}_2\text{O}$ appears to represent most simply and correctly the reaction which occurs. The maximum yield obtained was about 28 per cent of the theoretical, and this method is of interest as being the first in which hydrazine is converted into hydrazoic acid in the absence of any other substance containing nitrogen. Other experiments show that small quantities of hydrazoic acid can be prepared by the action of certain other oxidation agents besides hydrogen peroxide upon hydrazine sulphate.

Quantitative Determination of Lead by Persulphates in Acid Solution.—M. Dittrich and A. Reise.—If a 10 per cent solution of pure ammonium persulphate is added to a solution of lead nitrate a white crystalline precipitate of lead sulphate is at first formed, but rapidly darkens, owing to the formation of the peroxide. After five hours the precipitate may be washed with dilute ammonium sulphate without any trace of lead going into solution, and on being ignited with addition of a drop of sulphuric acid it goes quantitatively into sulphate. This method of precipitation is far more convenient than the ordinary method with sulphuric acid and alcohol. The solution need not stand so long, and, moreover, the lengthy processes of washing with alcohol and expelling the latter are avoided. The precipitation and conversion into PbO_2 are greatly accelerated if some silver nitrate is present in the lead solution, filtration being then possible after heating to 80° on the water-bath for three hours. On addition of hydrochloric acid to the precipitate chlorine is evolved, and in the solution obtained only traces of sulphate are to be detected; it is, however, not possible to convert all the precipitate into peroxide, even on heating and adding more persulphate. Apparently a silver peroxide is formed which very readily gives up oxygen for the oxidation of the lead, and at once takes up more oxygen from the persulphate.

Aceto-sulphates of Cellulose.—C. F. Cross, E. J. Bevan, and J. F. Briggs.—By the action of glacial acetic

acid, acetic anhydride, and sulphuric acid upon cellulose a neutral ester cellulose aceto-sulphate is formed. This compound is characterised by the resistance of the SO_4 residue towards alkaline saponification agents, while it is exceedingly readily hydrated. The substance when dried in air contains 8 per cent of hygroscopic moisture, and thus forms an important exception to the general rule which holds good for other series of cellulose esters. By altering the proportion of H_2SO_4 to the acetic acid anhydride mixture, instead of the normal cellulose, aceto-sulphate products soluble in water are obtained; these contain a higher percentage of combined SO_4 than the insoluble product. The soluble esters show well-defined colloid properties; they can be salted out from the solution, and thus separated as gelatinous precipitates. The normal ester is soluble in dilute alcohol. From quantitative saponification experiments it is found that the esters are formed according to the equation—



Thus the proportion $4\text{C}_6\text{H}_{10}\text{O}_5 : \text{H}_2\text{SO}_4$ shows that cellulose in its reactions must behave like a complex with at least 24 carbon atoms. Even when combined with a dibasic acid, the cellulose complex retains unimpaired its character of a homogeneous compound; the authors' researches do not show that a selective molecular action takes place, or a splitting up of the original cellulose aggregate.

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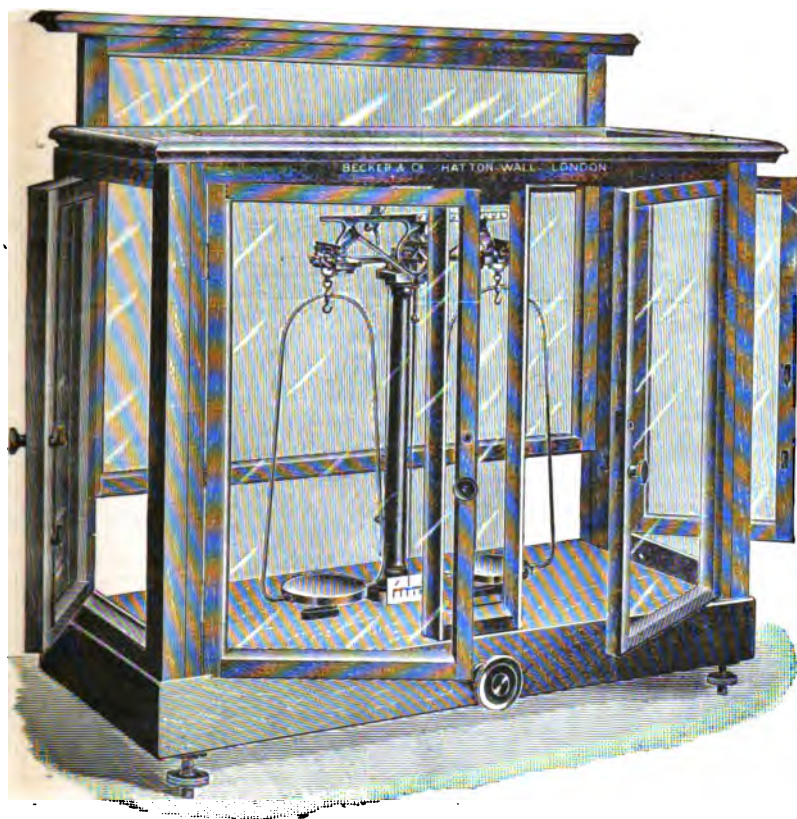
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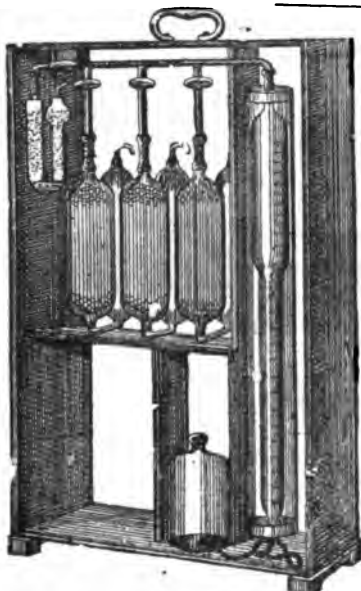
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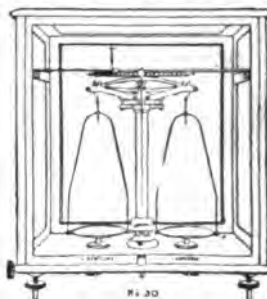
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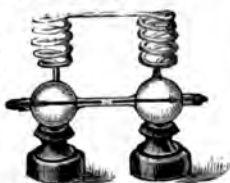
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THE CHEMICAL NEWS.

VOL. XCII., No. 2386.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SOUTH AFRICA, 1905.

FIRST PART OF ADDRESS OF THE PRESIDENT,
Professor G. H. DARWIN, M.A., LL.D., Ph.D., F.R.S.
(Delivered at CAPE TOWN, August 15th).

BARTHOLOMEU DIAZ, the discoverer of the Cape of Storms, spent sixteen months on his voyage, and the little flotilla of Vasco de Gama, sailing from Lisbon on July 8, 1497, only reached the Cape in the middle of November. These bold men, sailing in their puny fishing smacks to unknown lands, met the perils of the sea and the attacks of savages with equal courage. How great was the danger of such a voyage may be gathered from the fact that less than half the men who sailed with de Gama lived to return to Lisbon. Four hundred and eight years have passed since that voyage, and a ship of 13,000 tons has just brought us here, in safety and luxury, in but little more than a fortnight!

How striking are the contrasts presented by these events! On the one hand, compare the courage, the endurance, and the persistence of the early navigators with the little that has been demanded of us; on the other hand, consider how much man's power over the forces of Nature has been augmented during the past four centuries. The capacity for heroism is probably undiminished, but certainly the occasions are now rarer when it is demanded of us. If we are heroes, at least but few of us ever find it out, and, when we read stories of ancient feats of courage, it is hard to prevent an uneasy thought that, notwithstanding our boasted mechanical inventions, we are perhaps degenerate descendants of our great predecessors.

Yet the thought that to-day is less romantic and less heroic than yesterday has its consolation, for it means that the lot of man is easier than it was. Mankind, indeed, may be justly proud that this improvement has been due to the successive efforts of each generation to add to the heritage of knowledge handed down to it by its predecessors, whereby we have been born to the accumulated endowment of centuries of genius and labour.

I am told that in the United States the phrase "I want to know" has lost the simple meaning implied by the words, and has become a mere exclamation of surprise. Such a conventional expression could hardly have gained currency except amongst a people who aspire to knowledge. The dominance of the European race in America, Australasia, and South Africa has no doubt arisen from many causes, but amongst these perhaps the chief one is that not only do "we want to know," but also that we are determined to find out. And now within the last quarter of a century we have welcomed into the ranks of those who "want to know" an oriental race, which has already proved itself strong in the peaceful arts of knowledge.

I take it, then, that you have invited us because you want to know what is worth knowing; and we are here because we want to know you, to learn what you have to tell us, and to see that South Africa of which we have heard so much.

The hospitality which you are offering us is so lavish, and the journeys which you have organised are so extensive, that the cynical observer might be tempted to describe our meeting as the largest picnic on record. Although we

intend to enjoy our picnic with all our hearts, yet I should like to tell the cynic, if he is here, that perhaps the most important object of these conferences is the opportunity they afford for personal intercourse between men of like minds who live at the remotest corners of the earth.

We shall pass through your land with the speed and the voracity of a flight of locusts; but, unlike the locust, we shall, I hope, leave behind us permanent fertilisation in the form of stimulated scientific and educational activity. And this result will ensue whether or not we who have come from Europe are able worthily to sustain the lofty part of prophets of science. We shall try our best to play to your satisfaction on the great stage upon which you call on us to act, and if when we are gone you shall, amongst yourselves, pronounce the performance a poor one, yet the fact will remain, that the meeting has embodied in a material form the desire that the progress of this great continent shall not be merely material; and such an aspiration secures its own fulfilment. However small may be the tangible results of our meeting, we shall always be proud to have been associated with you in your efforts for the advancement of science.

We do not know whether the last hundred years will be regarded for ever as the *sacculum mirabile* of discovery, or whether it is but the prelude to yet more marvellous centuries. To us living men, who scarcely pass a year of our lives without witnessing some new marvel of discovery or invention, the rate at which the development of knowledge proceeds is truly astonishing; but from a wider point of view the scale of time is relatively unimportant, for the universe is leisurely in its procedure. Whether the changes which we witness be fast or slow, they form a part of a long sequence of events which begin in some past of immeasurable remoteness, and tend to some end which we cannot foresee. It must always be profoundly interesting to the mind of man to trace successive cause and effect in the chain of events which make up the history of the earth and all that lives on it, and to speculate on the origin and future fate of animals, and of planets, suns, and stars. I shall try, then, to set forth in my Address some of the attempts which have been made to formulate evolutionary speculation. This choice of a subject has, moreover, been almost forced on me by the scope of my own scientific work, and it is, I think, justified by the name which I bear. It will be my fault and your misfortune if I fail to convey to you some part of the interest which is naturally inherent in such researches.

The man who propounds a theory of evolution is attempting to re-construct the history of the past by means of the circumstantial evidence afforded by the present. The historian of man, on the other hand, has the advantage over the evolutionist in that he has the written records of the past on which to rely. The discrimination of the truth from amongst discordant records is frequently a work demanding the highest qualities of judgment; yet when this end is attained it remains for the historian to convert the arid skeleton of facts into a living whole by clothing it with the flesh of human motives and impulses. For this part of his task he needs much of that power of entering into the spirit of other men's lives which goes to the making of a poet. Thus the historian should possess not only the patience of the man of science in the analysis of facts, but also the imagination of the poet to grasp what the facts have meant. Such a combination is rarely to be found in equal perfection on both sides, and it would not be hard to analyse the works of great historians so as to see which quality was predominant in each of them.

The evolutionist is spared the surpassing difficulty of the human element, yet he also needs imagination, although of a different character from that of the historian. In its lowest form his imagination is that of the detective who re-constructs the story of a crime; in its highest it demands the power of breaking loose from all the trammels of convention and education, and of imagining something which has never occurred to the mind of man before. In every case the evolutionist must form a theory for the facts before

him, and the great theorist is only to be distinguished from the fantastic fool by the sobriety of his judgment—a distinction, however, sufficient to make one rare and the other only too common.

The test of a scientific theory lies in the number of facts which it groups into a connected whole; it ought besides to be fruitful in pointing the way to the discovery and co-ordination of new and previously unsuspected facts. Thus a good theory is in effect a cyclopædia of knowledge, susceptible of indefinite extension by the addition of supplementary volumes.

Hardly any theory is all true, and many are not all false. A theory may be essentially at fault, and yet point the way to truth, and so justify its temporary existence. We should not, therefore, totally reject one or other of two rival theories on the ground that they seem, with our present knowledge, mutually inconsistent, for it is likely that both may contain important elements of truth. The theories of which I shall have to speak hereafter may often appear discordant with one another according to our present lights. Yet we must not scruple to pursue the several divergent lines of thought to their logical conclusions, relying on future discovery to eliminate the false and to reconcile together the truths which form part of each of them.

In the mouths of the unscientific evolution is often spoken of as almost synonymous with the evolution of the various species of animals on the earth, and this again is sometimes thought to be practically the same thing as the theory of Natural Selection. Of course those who are conversant with the history of scientific ideas are aware that a belief in the gradual and orderly transformation of Nature, both animate and inanimate, is of great antiquity.

We may liken the facts on which theories of evolution are based to a confused heap of beads, from which a keen-sighted searcher after truth picks out and strings together a few which happen to catch his eye, as possessing certain resemblances. Until recently, theories of evolution in both realms of Nature were partial and discontinuous, and the chains of facts were correspondingly short and disconnected. At length the theory of Natural Selection, by formulating the cause of the divergence of forms in the organic world from the parental stock, furnished the naturalist with a clue by which he examined the disordered mass of facts before him, and he was thus enabled to go far in deducing order where chaos had ruled before, but the problem of reducing the heap to perfect order will probably baffle the ingenuity of the investigator for ever.

So illuminating has been this new idea that, as the whole of Nature has gradually been re-examined by its aid, thousands of new facts have been brought to light, and have been strung in due order on the necklace of knowledge. Indeed, the transformation resulting from the new point of view has been so far-reaching as almost to justify the misapprehension of the unscientific as to the date when the doctrines of evolution first originated in the mind of man.

It is not my object, nor indeed am I competent, to examine the extent to which the theory of Natural Selection has needed modification since it was first formulated by my father and Wallace. But I am surely justified in maintaining that the general principle holds its place firmly as a permanent acquisition to modes of thought.

Evolutionary doctrines concerning inanimate Nature, although of much older date than those which concern life, have been profoundly affected by the great impulse of which I have spoken. It has thus come about that the origin and history of the chemical elements and of stellar systems now occupy a far larger space in the scientific mind than was formerly the case. The subject which I shall discuss to-night is the extent to which ideas, parallel to those which have done so much towards elucidating the problems of life, hold good also in the world of matter; and I believe that it will be possible to show that in this respect there exists a resemblance between the two realms of Nature, which is not merely fanciful. It is proper

to add that as long ago as 1873 Baron Karl du Prel discussed the same subject from a similar point of view, in a book entitled "The Struggle for Life in the Heavens" ("Der Kampf um's Dasein am Himmel," zweite Auflage, Denicke, Berlin, 1876).

Although inanimate matter moves under the action of forces which are incomparably simpler than those governing living beings, yet the problems of the physicist and the astronomer are scarcely less complex than those which present themselves to the biologist. The mystery of life remains as impenetrable as ever, and in his evolutionary speculations the biologist does not attempt to explain life itself, but, adopting as his unit the animal as a whole, discusses its relationships to other animals and to the surrounding conditions. The physicist, on the other hand, is irresistibly impelled to form theories as to the intimate constitution of the ultimate parts of matter, and he desires further to piece together the past histories and the future fates of planets, stars, and nebulae. If then the speculations of the physicist seem in some respects less advanced than those of the biologist, it is chiefly because he is more ambitious in his aims. Physicists and astronomers have not yet found their Johannesburg or Kimberley; but, although we are still mere prospectors, I am proposing to show you some of the dust and diamonds which we have already extracted from our surface mines.

The fundamental idea in the theory of Natural Selection is the persistence of those types of life which are adapted to their surrounding conditions, and the elimination by extermination of ill-adapted types. The struggle for life amongst forms possessing a greater or less degree of adaptation to slowly varying conditions is held to explain the gradual transmutation of species. Although a different phraseology is used when we speak of the physical world, yet the idea is essentially the same.

The point of view from which I wish you to consider the phenomena of the world of matter may be best explained if, in the first instance, I refer to political institutions, because we all understand, or fancy we understand, something of politics, whilst the problems of physics are commonly far less familiar to us. This illustration will have a further advantage in that it will not be a mere parable, but will involve the fundamental conception of the nature of evolution.

The complex interactions of man with man in a community are usually described by such comprehensive terms as the State, the Commonwealth, or the Government. Various States differ widely in their constitution and in the degree of the complexity of their organisation, and we classify them by various general terms, such as autocracy, aristocracy, or democracy, which express somewhat loosely their leading characteristics. But, for the purpose of showing the analogy with physics, we need terms of wider import than those habitually used in politics. All forms of the State imply inter-relationship in the actions of men, and action implies movement. Thus the State may be described as a configuration or arrangement of a community of men; or we may say that it implies a definite mode of motion of man—that is to say, an organised scheme of action of man on man. Political history gives an account of the gradual changes in such configurations or modes of motion of men as have possessed the quality of persistence or of stability to resist the disintegrating influence of surrounding circumstances.

In the world of life the naturalist describes those forms which persist as species; similarly the physicist speaks of stable configurations or modes of motion of matter; and the politician speaks of States. The idea at the base of all these conceptions is that of stability, or the power of resisting disintegration. In other words, the degree of persistence or permanence of a species, of a configuration of matter, or of a State depends on the perfection of its adaptation to its surrounding conditions.

If we trace the history of a State we find the degree of its stability gradually changing, slowly rising to a maximum, and then slowly declining. When it falls to nothing a

revolution ensues, and a new form of government is established. The new mode of motion or government has at first but slight stability, but it gradually acquires strength and permanence, until in its turn the slow decay of stability leads on to a new revolution.

Such crises in political history may give rise to a condition in which the State is incapable of perpetuation by transformation. This occurs when a savage tribe nearly exterminates another tribe, and leads the few survivors into slavery; the previous form of government then becomes extinct.

The physicist, like the biologist and the historian, watches the effect of slowly varying external conditions; he sees the quality of persistence or stability gradually decaying until it vanishes, when there ensues what is called, in politics, a revolution.

These considerations lead me to express a doubt whether biologists have been correct in looking for continuous transformation of species. Judging by analogy we should rather expect to find slight continuous changes occurring during a long period of time, followed by a somewhat sudden transformation into a new species, or by rapid extinction. However this may be, when the stability of a mode of motion vanishes, the physicist either finds that it is replaced by a new persistent type of motion adapted to the changed conditions, or perhaps that no such transformation is possible, and that the mode of motion has become extinct. The evanescent type of animal life has often been preserved for us, fossilised in geological strata; the evanescent form of government is preserved in written records or in the customs of savage tribes; but the physicist has to pursue his investigations without such useful hints as to the past.

The time-scale in the transmutation of species of animals is furnished by the geological record, although it is not possible to translate that record into years. As we shall see hereafter, the time needed for a change of type in atoms or molecules may be measured by millionths of a second, while in the history of the stars continuous changes occupy millions of years. Notwithstanding this gigantic contrast in speed, yet the process involved seems to be essentially the same.

It is hardly too much to assert that, if the conditions which determine stability of motion could be accurately formulated throughout the universe, the past history of the cosmos and its future fate would be unfolded. How indefinitely far we stand removed from such a state of knowledge will become abundantly clear from the remainder of my Address.

The study of stability and instability then furnishes the problems which the physicist and biologist alike attempt to solve. The two classes of problems differ principally in the fact that the conditions of the world of life are so incomparably more intricate than those of the world of matter that the biologist is compelled to abandon the attempt to determine the absolute amount of the influence of the various causes which have affected the existence of species. His conclusions are merely qualitative and general, and he is almost universally compelled to refrain from asserting even in general terms what are the reasons which have rendered one form of animal life stable and persistent, and another unstable and evanescent.

On the other hand, the physicist, as a general rule, does not rest satisfied unless he obtains a quantitative estimate of various causes and effects on the systems of matter which he discusses. Yet there are some problems of physical evolution in which the conditions are so complex that the physicist is driven, as is the biologist, to rest satisfied with qualitative rather than quantitative conclusions. But he is not content with such crude conclusions except in the last resort, and he generally prefers to proceed by a different method.

The mathematician mentally constructs an ideal mechanical system or model, which is intended to represent in its leading features the system he wants to examine. It is often a task of the utmost difficulty to devise such a

model, and the investigator may perchance unconsciously drop out as unimportant something which is really essential to represent actuality. He next examines the conditions of his ideal system, and determines, if he can, all the possible stable and unstable configurations, together with the circumstances which will cause transitions from one to the other. Even when the working model has been successfully imagined, this latter task may often overtax the powers of the mathematician. Finally, it remains for him to apply his results to actual matter, and to form a judgment of the extent to which it is justifiable to interpret Nature by means of his results.

The remainder of my Address will be occupied by an account of various investigations which will illustrate the principles and methods which I have now explained in general terms.

The fascinating idea that matter of all kinds has a common substratum is of remote antiquity. In the Middle Ages the alchemists, inspired by this idea, conceived the possibility of transforming the baser metals into gold. The sole difficulty seemed to them the discovery of an appropriate series of chemical operations. We now know that they were always indefinitely far from the goal of their search, yet we must accord to them the honour of having been the pioneers of modern chemistry.

The object of alchemy, as stated in modern language, was to break up or dissociate the atoms of one chemical element into its component parts, and afterwards to reunite them into atoms of gold. Although even the dissociative stage of the alchemistic problem still lies far beyond the power of the chemist, yet modern researches seem to furnish a sufficiently clear idea of the structure of atoms to enable us to see what would have to be done to effect a transformation of elements. Indeed, in the complex changes which are found to occur spontaneously in uranium, radium, and the allied metals we are probably watching a spontaneous dissociation and transmutation of elements.

Natural Selection may seem, at first sight, as remote as the poles asunder from the ideas of the alchemist, yet dissociation and transmutation depend on the instability and regained stability of the atom, and the survival of the stable atom depends on the principle of Natural Selection.

Until some ten years ago the essential diversity of the chemical elements was accepted by the chemist as an ultimate fact, and indeed the very name of atom, or that which cannot be cut, was given to what was supposed to be the final indivisible portion of matter. The chemist thus proceeded in much the same way as the biologist who, in discussing evolution, accepts the species as his working unit. Accordingly, until recently the chemist discussed working models of matter of atomic structure, and the vast edifice of modern chemistry has been built with atomic bricks.

But within the last few years the electrical researches of Lenard, Röntgen, Becquerel, the Curies, of my colleagues Larmor and Thomson, and of a host of others, have shown that the atom is not indivisible, and a flood of light has been thrown thereby on the ultimate constitution of matter. Amongst all these fertile investigators it seems to me that Thomson stands pre-eminent, because it is principally through him that we are to-day in a better position for picturing the structure of an atom than was ever the case before.

Even if I had the knowledge requisite for a complete exposition of these investigations, the limits of time would compel me to confine myself to those parts of the subject which bear on the constitution and origin of the elements.

It has been shown, then, that the atom, previously supposed to be indivisible, really consists of a large number of component parts. By various convergent lines of experiment it has been proved that the simplest of all atoms—namely, that of hydrogen—consists of about 800 separate parts; while the number of parts in the atom of the denser metals must be counted by tens of thousands.

These separate parts of the atom have been called corpuscles or electrons, and may be described as particles of negative electricity. It is paradoxical, yet true, that the physicist knows more about these ultra-atomic corpuscles, and can more easily count them than is the case with the atoms of which they form the parts.

The corpuscles, being negatively electrified, repel one another just as the hairs on a person's head mutually repel one another when combed with a vulcanite comb. The mechanism is as yet obscure whereby the mutual repulsion of the negative corpuscles is restrained from breaking up the atom, but a positive electrical charge, or something equivalent thereto, must exist in the atom, so as to prevent disruption. The existence in the atom of this community of negative corpuscles is certain, and we know further that they are moving with speeds which may in some cases be comparable to the velocity of light, namely, 200,000 miles a second. But the mechanism whereby they are held together in a group is hypothetical.

It is only just a year ago that Thomson suggested, as representing the atom, a mechanical or electrical model whose properties could be accurately examined by mathematical methods. He would be the first to admit that his model is at most merely a crude representation of actuality, yet he has been able to show that such an atom must possess mechanical and electrical properties which simulate, with what Whetham describes as "almost Satanic exactness," some of the most obscure and yet most fundamental properties of the chemical elements. "Se non è vero, è ben trovato," and we are surely justified in believing that we have the clue which the alchemists sought in vain.

Thomson's atom consists of a globe charged with positive electricity, inside which there are some thousand or thousands of corpuscles of negative electricity, revolving in regular orbits with great velocities. Since two electrical charges repel one another if they are of the same kind, and attract one another if they are of opposite kinds, the corpuscles mutually repel one another, but all are attracted by the globe containing them. The forces called into play by these electrical interactions are clearly very complicated, and you will not be surprised to learn that Thomson found himself compelled to limit his detailed examination of the model atom to one containing about seventy corpuscles. It is indeed a triumph of mathematical power to have determined the mechanical conditions of such a miniature planetary system as I have described.

It appears that there are definite arrangements of the orbits in which the corpuscles must revolve, if they are to be persistent or stable in their motions. For the purpose of general discussion, which is all that I shall attempt, you may take it that the number of corpuscles in such a community is fixed; and we may state that definite numbers of corpuscles are capable of association in stable communities of definite types.

An infinite number of communities are possible, possessing greater or lesser degrees of stability. Thus the corpuscles in one such community might make thousands of revolutions in their orbits before instability declared itself; such an atom might perhaps last for a long time as estimated in millions of seconds, but it must finally break up, and the corpuscles must disperse or re-arrange themselves after the ejection of some of their number. We are thus led to conjecture that the several chemical elements represent those different kinds of communities of corpuscles which have proved by their stability to be successful in the struggle for life. If this is so, it is almost impossible to believe that the successful species have existed for all time, and we must hold that they originated under conditions about which I must forbear to follow Sir Norman Lockyer in speculating.

But if the elements were not eternal in the past, we must ask whether there is reason to believe that they will be eternal in the future. Now, although the conception of the decay of an element and its spontaneous transmutation into another element would have seemed absolutely repugnant to the chemist until recently, yet analogy with other

moving systems seems to suggest that the elements are not eternal.

At any rate it is of interest to pursue to its end the history of the model atom which has proved to be so successful in imitating the properties of matter. The laws which govern electricity in motion indicate that such an atom must be radiating or losing energy, and therefore a time must come when it will run down, as a clock does. When this time comes it will spontaneously transmute itself into an element which needs less energy than was required in the former state. Thomson conceives that an atom might be constructed after his model so that its decay should be very slow. It might, he thinks, be made to run for a million years, but it would not be eternal.

Such a conclusion is an absolute contradiction to all that was known of the elements until recently, for no symptoms of decay are perceived, and the elements existing in the solar system must already have lasted for millions of years. Nevertheless, there is good reason to believe that in radium, and in other elements possessing very complex atoms, we do actually observe that break-up and spontaneous rearrangement which constitute a transmutation of elements.

It is impossible as yet to say how science will solve this difficulty, but future discovery in this field must surely prove deeply interesting. It may well be that the train of thought which I have sketched will ultimately profoundly affect the material side of human life, however remote it may now seem from our experiences of daily life.

I have not as yet made any attempt to represent the excessive minuteness of the corpuscles, of whose existence we are now so confident; but, as an introduction to what I have to speak of next, it is necessary to do so. To obtain any adequate conception of their size we must betake ourselves to a scheme of threefold magnification. Lord Kelvin has shown that, if a drop of water were magnified to the size of the earth, the molecules of water would be of a size intermediate between that of a cricket-ball and of a marble. Now each molecule contains three atoms, two being of hydrogen and one of oxygen. The molecular system probably presents some sort of analogy with that of a triple star; the three atoms, replacing the stars, revolving about one another in some sort of dance which cannot be exactly described. I doubt whether it is possible to say how large a part of the space occupied by the whole molecule is occupied by the atoms; but perhaps the atoms bear to the molecule some such relationship as the molecule to the drop of water referred to. Finally, the corpuscles may stand to the atom in a similar scale of magnitude. Accordingly a threefold magnification would be needed to bring these ultimate parts of the atom within the range of our ordinary scales of measurement.

I have already considered what would be observed under the triply powerful microscope, and must now return to the intermediate stage of magnification, in which we consider those communities of atoms which form molecules. This is the field of research of the chemist. Although prudence would tell me that it would be wiser not to speak of a subject of which I know so little, yet I cannot refrain from saying a few words.

The community of atoms in water has been compared with a triple star, but there are others known to the chemist in which the atoms are to be counted by fifties and hundreds, so that they resemble constellations.

I conceive that here again we meet with conditions similar to those which we have supposed to exist in the atom. Communities of atoms are called chemical combinations, and we know that they possess every degree of stability. The existence of some is so precarious that the chemist in his laboratory can barely retain them for a moment; others are so stubborn that he can barely break them up. In this case dissociation and reunion into new forms of communities are in incessant and spontaneous progress throughout the world. The more persistent or more stable combinations succeed in their struggle for life, and are found in vast quantities, as in the cases of common salt and of the combinations of silicon. But no one has

ever found a mine of gun-cotton, because it has so slight a power of resistance. If, through some accidental collocation of elements, a single molecule of gun-cotton were formed, it would have but a short life.

Stability is, further, a property of relationship to surrounding conditions; it denotes adaptation to environment. Thus salt is adapted to the struggle for existence on the earth, but it cannot withstand the severer conditions which exist in the sun.

[The President here announced that he proposed to consider various theories of evolution in the heavens in the second portion of his Address, to be delivered at Johannesburg on Wednesday, August 30].

A SIMPLE METHOD OF SHOWING THE PRESENCE OF THE HELIUM FORMED FROM RADIUM BROMIDE.

By F. GIESEL.

THE detonating gas evolved from radium bromide solutions, like that expelled from crystallised aqueous radium bromide, owes its activity to traces of admixed emanation. Ramsay's discovery has proved the truth of the conjecture I have previously expressed (*Berichte*, 1902, xxxv., 3608), that we should obtain an insight into the internal processes of the radium atom if it was possible to prove the existence of a gas arising from the radium (and not from the water). The fact that only a few have succeeded in proving the presence of helium is due to the exceedingly small quantities of emanation which are formed, and to the difficulty of separating the helium in a pure state from the large quantities of detonating gas.

In order to overcome these difficulties, I put 50 m.grms. of anhydrous radium bromide into each of two Geissler tubes (1 and 2) of the ordinary form with aluminium electrodes, and exhausted as completely as possible, firstly to prevent the formation of detonating gas, and secondly to see whether the presence of water has any influence on the formation of emanation or helium. Tube 1 contained about 5 c.c., tube 2 about 15 c.c.; the first contained the salt heated to a temperature only just below its melting-point for the purpose of dehydration, and the second contained the same salt melted on a platinum wire. In tube 1, though it was heated for hours with an induction current, it was not possible to obtain such a vacuum that the luminescence of the gaseous residues in the capillary tube ceased, but was far better with tube 2. After melting off the pump the hydrogen and mercury lines were very plainly visible in tube 1 and only faintly visible in tube 2. After two months the helium line $D_3 = \lambda 587.6$ appeared in tube 1, and after six months $\lambda 502$ appeared, and also $\lambda 495$, $\lambda 470$, $\lambda 446^*$ very faintly. With tube 2, which luminesced only faintly, only the D_3 line could be perceived after this lapse of time. The lines were identified by means of a spectroscopic of high dispersion by comparison with the aid of a cross-thread arrangement.

The induction current can be driven through both tubes for any length of time without affecting the helium spectrum. No change in the gas pressure of the tubes could be observed as far as can be judged by the luminescence phenomena.

It may be mentioned as a striking fact that the activity of the gas appears very small as compared with that of the detonating gas from radium solutions. The emanation thus appears to be retained firmly by the dehydrated radium bromide.

The changes of the gaseous contents of the tubes will be further examined.—*Berichte*, 1905, xxxviii., 2299.

ON THE RETROGRESSION OF SOLUBLE PHOSPHATES IN MIXED MANURES.

By GEORGE GRAY, F.C.S., Lecturer on Chemistry, Canterbury Agricultural College, Lincoln, N.Z.

THE term "retrogression" applied to superphosphate of lime implies certain chemical changes by which the soluble mono-calcic phosphate is converted into an insoluble form.

The chief advantages possessed by superphosphate over other forms of phosphatic manure lies in the fact that the phosphoric anhydride, being in a soluble form of combination, is better distributed through the soil, and brought more within the range of plant roots. In well-made superphosphate the retrogression is but small, but in cases where insufficient sulphuric acid has been employed and the raw tri-calcic phosphate is but partially decomposed, the degree of retrogression may be considerable. In the presence of undecomposed tri-calcic phosphate, mono-calcic phosphate is reduced to the condition of di-calcic phosphate. In cases where the original phosphate contains much calcic carbonate, and where a portion of this remains undecomposed, or where superphosphate is mixed with other manures containing calcic carbonate, the retrogression may proceed further, and tri-calcic phosphate may be formed. When iron is present in the raw phosphate, either as silicate or as pyrites, no action occurs; but when in the form of ferric or ferrous oxide, these form the corresponding sulphates, which react on the mono-calcic phosphate, and the retrogression is of a more serious nature. Alumina when present also causes retrogression, but the reactions are similar to those with calcium compounds. The retrograded phosphates are insoluble in water, but soluble in solutions of ammoniac citrate, and hence the term "citrate-soluble phosphates" frequently applied.

Considerable difference of opinion exists as to the agricultural value of these citrate-soluble phosphates, some agricultural chemists regarding them as being of equal value to the mono-calcic phosphate, while others consider them only of value equal to tri-calcic phosphate. Considering that the diffusive power of the phosphoric acid present has been destroyed, my own practice has been to value them only as tri-calcic phosphate. Manufacturers generally argue that, as the tri-calcic phosphate has been rendered once soluble at their expense, they should receive credit for it, while agriculturists maintain that it is only fair that they should pay a higher price for the phosphoric acid actually existing in the soluble form, and that the retrograde phosphate should be assessed at a lower value.

In the blending of manures, such as is largely done by our freezing companies, mistakes are often made, and the value of the superphosphate used considerably reduced by retrogression. Farmers, again, by mixing superphosphate with other substances in order to improve the mechanical texture, and to cause the manure to pass more easily through the drill, often completely destroy the soluble phosphate for which they have paid an increased price, the comparative market value of the soluble to the insoluble phosphate being about 100—63.

The object of the present investigation was to ascertain the nature of the retrogression, and the rate at which it proceeds in mixtures of superphosphate and other manures such as have come under notice as having been used in actual practice. In the experiments a good, well-made superphosphate was employed, containing "soluble" phosphate equal to 17.74 per cent of phosphoric anhydride. This was mixed with equal parts of other manures and the amounts of water-soluble, citrate-soluble, and insoluble phosphate determined from time to time. Briefly, the method of analysis consisted in extracting the mixtures with pure water, and afterwards with a neutral solution of ammonium citrate, determining the total phosphoric anhydride, that soluble in water, and that insoluble in ammonium citrate, the citrate soluble being taken by

* Himstedt and G. Meyer (*Berichte d. Naturf. Ges.*, at Freiburg, t. B, xvi., 10, May, 1905) have recently arrived at the same results by using dehydrated radium bromide in an electrodeless quartz tube with Tesla currents.

TABLE I.—Showing Retrogression of Soluble Phosphoric Anhydride in Mixed Manures.

	Original mixture.	Three hours.	Twenty four hours.	Six days.	Twelve days.	Eighteen days.
1. A Mixture of equal parts of Superphosphate and Bone-dust :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	8·87	8·87	8·87	8·62	8·62
Citrate-soluble	1·57	3·45	3·95	3·70	3·95	3·95
Insoluble	9·63	7·75	7·25	7·50	7·50	7·50
Total	20·07	20·07	20·07	20·07	20·07	20·07
2. Equal parts of Superphosphate and Coral Queen Guano :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	8·87	8·57	8·37	8·37	8·25
Citrate-soluble	3·43	10·89	7·94	9·64	8·64	8·26
Insoluble	12·96	5·50	8·75	7·25	8·25	8·75
Total	25·26	25·26	25·26	25·26	25·26	25·26
3. Equal parts of Superphosphate and Chesterfield Guano :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	7·87	7·37	4·87	4·00	3·37
Citrate-soluble	2·24	1·95	1·45	3·70	3·32	4·70
Insoluble	8·21	9·50	10·50	10·75	12·00	11·25
Total	19·32	19·32	19·32	19·32	19·32	19·32
4. Equal parts of Superphosphate and Basic Slag :—						
Phosphoric anhydride—Soluble in water.. ..	9·43	4·00	2·12	1·37	1·25	1·12
Citrate-soluble	2·49	15·67	16·05	14·80	15·92	14·80
Insoluble	10·25	2·50	4·00	6·00	5·00	6·25
Total	22·17	22·17	22·17	22·17	22·17	22·17
5. Equal parts of Superphosphate and Kainit :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	8·87	8·87	8·50	8·25	8·25
Citrate-soluble	0·72	1·75	1·75	0·62	1·62	2·37
Insoluble	1·03	0·00	0·00	1·50	0·75	0·00
Total	10·62	10·62	10·62	10·62	10·62	10·62
6. Equal parts of Superphosphate and Slaked Lime :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	0·50	0·00	0·00	0·00	0·00
Citrate-soluble	0·72	7·37	10·62	6·87	7·87	6·62
Insoluble	1·03	2·75	0·00	3·74	2·75	4·00
Total	10·62	10·62	10·62	10·62	10·62	10·62
7. Equal parts of Superphosphate and Ground Lime-stone :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	7·87	1·75	1·12	0·75	1·25
Citrate-soluble	0·72	2·03	8·15	8·78	9·15	8·65
Insoluble	1·06	0·75	0·75	0·75	0·75	0·75
Total	10·65	10·65	10·65	10·65	10·65	10·65

TABLE II.—Showing Percentage of Total Soluble Phosphoric Anhydride Reduced.

Mixture.	Three hours.	Twenty-four hours.	Six days.	Twelve days.	Eighteen days.
1. Superphosphate and bone-dust ..	0·0	0·0	0·0	2·8	2·8
2. Superphosphate and Coral Queen guano	0·0	3·3	5·3	5·3	7·0
3. Superphosphate and Chesterfield guano	11·2	16·9	44·8	54·9	62·0
4. Superphosphate and basic slag ..	57·6	77·5	85·4	86·7	88·1
5. Superphosphate and kainit	0·0	0·0	4·1	6·9	6·9
6. Superphosphate and slaked lime ..	94·3	100·0	100·0	100·0	100·0
7. Superphosphate and crushed lime-stone	11·2	80·2	87·3	91·5	85·9

difference. The method of determining citrate-soluble phosphoric anhydride is not by any means a satisfactory one, but still it is the best in use. Ammonic citrate solution, even when neutral, attacks the various forms of

phosphates in different degrees. Thus the manures used in the present case were found to yield to neutral ammonic citrate solution proportions of tri-calcic phosphate equivalent to phosphoric anhydride as follows:—

Bone-dust, 9 per cent of total phosphoric anhydride; Chesterfield guano, 17.5 per cent; Coral Queen guano, 18.5 per cent; basic slag, 16.4 per cent.

Table I. shows the condition of the phosphoric anhydride on first mixing the manures, and at intervals afterwards. The results are all expressed as phosphoric anhydride.

Table II. shows the percentage of the total phosphoric anhydride present that has retrograded during different periods.

Superphosphate and Bone-dust.—In this mixture the amount of retrogression is small, and proceeds but slowly. The citrate-soluble phosphoric anhydride is increased at the expense of the insoluble phosphate. This is probably due to the solvent action of ammonium citrate on tri-calcic phosphate before mentioned. The low degree of retrogression in the case of the bone-dust mixture may to some extent be due to the protection of the tri-calcic phosphate afforded by the ossein present. Doubtless bone-dust is the best form in which to use tri-calcic phosphate for mixing with superphosphate.

Superphosphate and Coral Queen Guano.—The sample of Coral Queen guano used contained 63.9 per cent of tri-calcic phosphate and 1.1 per cent of calcic carbonate, together with about 8.8 per cent of iron oxide. Like bone-dust, this manure appears to be slow in its action, only 7 per cent of the soluble phosphoric anhydride being reduced after eighteen days. The amount of citrate-soluble phosphate is considerably above that, due to retrogression, as in the case of bone dust, and the proportion is higher than that in the latter, due to the greater solvent action of the citrate solution on the guano.

Superphosphate and Chesterfield Guano.—This guano is characteristic in containing a high percentage of calcic carbonate (37.9 per cent), and, as may be expected, retrogression is considerable, and has proceeded not only to the stage di-calcic phosphate, but beyond this, to form insoluble tri-calcic phosphate.

Superphosphate and Basic Slag.—The influence of basic slag on superphosphate is due to two causes—the action of calcic oxide and the action of proto- and per-salts of iron. As is shown later, calcic oxide is very active in retrogression, and the oxides of iron produce reduction of the worst kind. Table II. shows that within three hours over 50 per cent of the acid was in an insoluble form. The production of phosphates of iron has increased the proportion of citrate-soluble compound considerably.

Superphosphate and Kainit.—The action of kainit is due mainly to the salts of magnesium present. The retrogression is small, only about 7 per cent of the acid being reduced in eighteen days.

Superphosphate and Slaked Lime.—The retrogression of superphosphate with slaked lime is particularly rapid, 94 per cent of the soluble phosphoric anhydride being reduced within three hours, and the whole amount present within twenty-four hours. When mixed considerable heat is evolved, and moisture evaporated. It is mainly the di-calcic phosphate that is formed at first, although probably with longer time this would further revert to the form of tri-calcic phosphate.

Superphosphate and Ground Limestone.—The effect of calcium carbonate, although not so great as that of slaked lime, is yet considerable. When mixed with superphosphate carbon dioxide is at once evolved, and within twenty-four hours 80 per cent of the phosphoric anhydride present is converted into a form in which it is soluble in ammoniac citrate.—*Transactions of the Australasian Association for the Advancement of Science*, 1904, p. 157.

Gentiopicroine.—Georges Tanret.—Gentiopicroine is a crystalline glucoside, hitherto almost unknown, which was discovered by Kromayer in the fresh root of gentian. It has since been prepared by a long and difficult series of manipulations. The author now discovers a simpler and more practical method for its preparation. After preparing it in a pure state, he investigates its properties and composition.—*Comptes Rendus*, cxli., No. 3.

NOTICES OF BOOKS

Spectroscopy. By E. C. C. BALY, F.I.C. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THE appearance at last of a really satisfactory text-book of spectroscopy will be heartily welcomed by the many who have had occasion to lament the non-existence of a book suited both for the use of the student as a text-book to be worked through, and also as a work of reference to be consulted on special points. For both purposes this book will be found excellent. The students who use it will derive the greater benefit from it because it is the work of a teacher who understands the difficulties and stumbling blocks which the most intelligent are bound to meet with, and while the treatment is by no means elementary the clearness of the author's style makes the book quite suitable for being put into the hands of those who have no previous acquaintance with the subject. Great attention is paid to the detailed description of the construction and manipulation of various instruments, the subject being presented specially from the practical point of view, but no branch is neglected, and the chapters on the more theoretical aspects form some of the most interesting parts of the book. The omission of set tables of wave-lengths enables the author to include much interesting and important matter which must otherwise have been sacrificed, and is hence quite justified. The book is fully and carefully illustrated throughout, and contains very complete diagrams and cuts of Rowland's grating ruling engines.

A Systematic Course of Practical Organic Chemistry. By LIONEL GUY RADCLIFFE, F.C.S., and FRANK STURDY SINNATT, F.C.S. London, New York, and Bombay: Longmans, Green, and Co. 1905.

ALTHOUGH this book possesses many valuable features, on the whole it cannot but be regarded as disappointing, and in spite of the fact that it can be recommended in default of a better, we consider that the ideal book on practical organic chemistry is yet to be written. The chief respects in which the book falls short are, firstly, the lack of such systematic arrangement as would enable the student to realise that organic chemistry is not merely a chaotic accumulation of unrelated facts, and secondly the failure to develop the originality of the student to the utmost extent, so that the book hardly seems likely to stimulate the spirit of research latent in the mind of the average young chemist. This latter defect is most noticeable in the special work for advanced students, which should have provided scope for the display of a little more enterprise on the part of the worker than is necessary for a few additional preparations and qualitative reactions. Apart from these shortcomings, which it possesses in common with so many of its rivals, the book has numerous good points. The directions for the experiments appear to be adequate without being redundant, and the repeated instructions to "weigh the yield," thus keeping the quantitative aspect of the reactions constantly before the worker, are an excellent feature. All illustrations are omitted, the authors believing that it is best to have set up in the laboratory a model of the apparatus to be used, or else to allow the students to submit sketches of what they consider suitable arrangements for the various experiments.

Report on the Manufacture of Paints and Colours containing Lead. By T. M. LEGGE, M.D., H.M. Medical Inspector of Factories. London: Darling and Son, Ltd. 1905.

IN this report of H.M. Medical Inspector of Factories the incidence of plumbism in paint and colour works is discussed, the statistics collected showing that most of the poisoning which occurs in such works is undoubtedly due

to the dust formed during the process of mixing and grinding white-lead. In view of the fact that at present very little is done to remove or even diminish this source of danger, the Inspector's recommendations regarding the regulations which should be enforced will be read with great interest; these suggested regulations are far less stringent than those which the German Federal Council decreed in 1903, and of which a translation is appended. The report is illustrated by photographs of paint-grinding machines and by diagrams showing various fan arrangements for removing white-lead dust in paint works.

Le Four Electrique, Son Origine, Ses Transformations, et Ses Applications. ("The Electric Furnace, its Origin, Transformations, and Applications"). By ADOLPHE MINET. (Part I.). Paris: A. Hermann. 1905.

THE increasing application of the electric furnace in many industrial processes has led to the production of important additions to the literature of the subject, of which additions this bids fair to be one of the most valuable. The author divides the history of the electric furnace into three periods; the first, from 1808 to 1886, he describes as the laboratory period, at the beginning of which the voltaic arc was discovered by Davy. Although towards the end of this period Borchers had invented a resistance furnace by means of which he had succeeded in reducing some refractory oxides, and Louis Clerc with an arc furnace had fused most of these oxides, the electric furnace in general had as yet found no applications outside the laboratory. The second period in the history lasts from 1886 to 1890, and sees the beginning of industrial applications which during the last period (1890 to the present day) have developed to such a striking extent. The present volume includes, first, a plan of the whole work, in which the parts played by the various investigators are briefly outlined. In this connection it is curious to notice that in the third period, in which we should have expected to find Moissan's name pre-eminent, it is only mentioned quite incidentally, though the value of Bullier's work is recognised. The rest of this part contains an account of the first period, which the author considers both from the descriptive and theoretical points of view; in the last chapters devoted to the theory, physical units, electrical systems and cycles, and the fundamental laws of electro-chemistry are discussed, and tables of various important constants are given. Although the subject, as far as this period is concerned, may be regarded as of little more than theoretical interest, the author has laid in this part the foundations of a most useful treatise, if the succeeding four volumes fulfil the promise of the first.

Les Nouveautés Chimiques pour 1905. ("Chemical Novelties for 1905"). By CAMILLE POULENC, Docteur ès Sciences. Paris: J. B. Baillière et Fils. 1905.

In this volume the author has followed the general plan adopted in the preparation of preceding volumes. It contains descriptions of the recent improvements and modifications which have been suggested with regard to various kinds of apparatus used in chemical work, dealing first with the general applications of physics to chemistry, which includes the discussion with illustrations of new apparatus for determining the physical properties of substances. The next section is devoted to more purely chemical operations, such as distillation, filtration, &c.; a good deal of space being somewhat unadvisedly given to the description of Verneuil's apparatus for the artificial production of rubies by fusion. The chapter on electro-chemistry includes all the apparatus employed by the Curies in the study of radio-activity, as well as Commelin and Viau's mixed accumulator. In the pages on analytical processes many useful novelties collected from all sources are described, and the analyst will be likely to glean many hints from it.

CORRESPONDENCE.

ZINC DUST.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of August 4th (vol. xcii., p. 56) appears a paper by A. B. Stevens on the above subject, which kindly allow me to supplement with a few observations of my own.

From Mr. Stevens' paper it might be inferred that zinc dust is of special manufacture; but, as is well known, it is a by-product, and although at the present moment it is in fair demand and the price comparable with that of regline zinc, it is not manufactured designedly.

It generally appears in commerce packed in old petroleum casks, from which it abstracts relatively large amounts of petroleum of a particularly disgusting odour; this is probably the source of the oil recovered by Mr. Stevens, and it is not, as the paper might suggest, a condensation product from the manufacture of the dust itself.

Quite recently I had to heat half a ton of zinc dust to 600° F. in a closed vessel, and the escaping gas and vapour had such an overpowering smell that I had to suspend operations until provision could be made to deal with it.

I have also remarked the evolution of ammonia on heating with caustic alkali, and on this account have discontinued the use of zinc dust in Kjeldahl operations, but since I failed to obtain ammonia when using caustic soda from metallic sodium, I ascribed it to the reduction of the ever-present nitrates in the commercial alkali.

I would also point out that almost everything in a laboratory becomes contaminated with ammonia unless well protected from the atmosphere, and that many finely-divided solids, such as zinc dust, have a special faculty for condensing vapours and gases, possibly acting like charcoal in this respect. It is almost inconceivable that a metallic body such as zinc dust should be able to fix atmospheric nitrogen; but when one considers that the normal atmosphere contains traces of ammonia, it is not surprising that the dust should absorb it on exposure to the air.

It is perhaps not generally known that zinc dust is sometimes pyrophoric, and if suspended in the air something like an explosion may occur if it becomes ignited. I have seen a 5-cwt. cask smoulder until it was converted into oxide to a depth of 4 or 5 inches, after which apparently it smothered itself out.

Under the microscope zinc dust is seen to consist of metallic globules 1 to 5 micromillimetres in diameter mixed with some oxide and impurities; if this oxide be removed by acid, washing, &c., the dust can be smelted down to regline metal if the air be excluded. Ordinary zinc dust cannot be so fused, but, under certain conditions, can be smelted into a curious crystalline mass, easily pulverable, and very brittle.—I am, &c.,

WILLIAM RAMSAY.

Birkenhead Iron Works, August 9, 1905.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 3, July 17, 1905.

Preparation of Binary Compounds of the Metals by means of Aluminium.—C. Matignon and R. Trannoy.—The authors prepare a number of phosphides, arsenides, silicides, and borides by application of the reducing properties of finely-divided aluminium.

Reduction of Thorium Oxide by means of Amorphous Boron, and Preparation of two Thorium Borides.—M. Binet du Jassonneix.—If an intimate mix-

ture of thorium and boron is heated in a charcoal crucible in the electric furnace, at a pressure of 100 volts and with current of 500 amperes, at the end of three minutes the mixture does not melt. It only melts when the current is increased to 700 amperes. Thorium bromides, shown by analysis to have the composition ThBr_6 and ThBr_4 , can then be separated from the melt.

Certain Reactions of Gaiac Resin.—P. Petit and M. Mayer.—The authors investigate the colour reaction given by gaiac resin, and find that tincture of gaiac gives a very strong blue colouration in presence of iron or manganese salts.

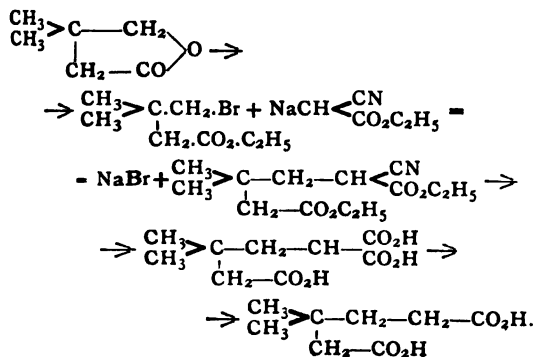
Action of Chloracetic Ethers on the Halogen-magnesium Derivatives of Orthotoluidine.—F. Bodroux.—Ethyl monochloracetate reacts energetically on magnesium orthotoluidine iodide. The author examines two special cases. 1. When the organo-magnesium salt is in ether solution, the orthoiodoacetoluide is formed almost quantitatively, $\text{CH}_3\text{—C}_6\text{H}_4\text{—NH—CO—CH}_2\text{I}$. 2. When, as sometimes happens, the organo-magnesium salt coagulates spontaneously, the yield of iodoacetoluide is small; the principal product of the operation in this case being ethyl iodacetate.

Action of Ethylamine and Isobutylamine on Cæsium.—E. Rengade.—The author's experiments show that the primary amines of the fatty series react on cæsium, giving as a final product a substituted amide; in the case of the first members of the series, an unstable ammonium compound is formed transitorily. Such derivatives are unstable; they decompose very easily when in contact with air at a temperature of about 110° . With water they give a cæsium hydrate, and the amine is formed again. The author also finds that it is very easy to pass from one of these amides to the others by the direct action of the corresponding amines or ammonia. Thus, liquefied ammonia dissolves cæsium ethylamide, but, after evaporation of excess of the liquid, crystals of cæsium amide remain. The loss of weight of the tube exactly corresponds to the substitution of CH_3 by H , $\text{CH}_3\text{NHCs} + \text{NH}_3 = \text{CH}_3\text{NH}_2 + \text{NH}_2\text{Cs}$.

Attempted Reduction in the Series of Dinitro-diphenylmethane Compounds.—H. Duval.—The author's experiments were made on dipara-aminodiphenylmethane purified by distillation in vacuo.

Condensation of Chloral with the Aromatic Hydrocarbons under the Influence of Aluminium Chloride.—Adolphe Dinesmann.—The author investigates the reaction of chloral on benzene, and finds that excellent yields are obtained under his experimental conditions, trichloromethylphenylcarbinol, $\text{C}_6\text{H}_5\text{—CHOH—CCl}_3$, being formed, resulting from the integral union of equal molecules of benzene and chloral. By repeating the reaction with toluene, paraxylene, and anisol, he shows the reaction to be of a general nature.

3,3-Dimethylbutyrolactone.—G. Blanc.—The author obtains the β -dimethyladipic acid, starting from M. Blaise's lactone, by the following series of transformations:—



Action of Tetrabromide of Acetylene and of Aluminium Chloride on Toluene.—James Lavaux.—The author investigates the theory of the reaction of a mixture of acetylene tetrabromide and aluminium chloride on toluene.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 8, 1905.

Higher Oxidation Products of Chromium.—E. H. Riesenfeld, H. E. Wohlers, and W. A. Kutsch.—Wiede has already prepared (blue) salts of the acid H_3CrO_7 . The author has now succeeded in obtaining the ammonium, sodium, and potassium salts of the higher acid, H_3CrO_8 , by cooling a mixture of water, 25 per cent alkali, and 50 per cent chromic acid anhydride solution, and adding, drop by drop, a 30 per cent solution of hydrogen peroxide. The temperature must not be allowed to exceed 0° . The solution darkens, and the red salt crystallises on the bottom of the vessel; the yield corresponds to about 50 per cent of the hydrogen peroxide used. The blue lower salts, e.g., $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$, are obtained similarly, but the chloride of the metal and hydrochloric acid are used instead of caustic alkali. The red salts, e.g., $(\text{NH}_4)_3\text{CrO}_8$, are very unstable, and readily give up oxygen, forming an amorphous powder. They are insoluble in pure alcohol and ether, but are decomposed, yielding chromate and aldehyde if more than 50 per cent of water is present in the alcohol. All three salts are slightly soluble in cold water. On warming in neutral and alkaline solutions, chromate is formed, while in strongly acid solution perchromic acid is produced, and is almost immediately for the most part converted into chromic salt. On heating the salts oxygen is slowly given up by the potassium salt at 170° , the sodium salt at 110° , and the ammonium salt at 40° ; when these temperatures are slightly exceeded, explosive decomposition takes place, and chromic oxide is formed. With concentrated sulphuric acid a violent reaction takes place, and chromous oxide is formed in green flakes. In the case of the ammonium salt, a blow will cause a sharp detonation.

Metallic Calcium.—K. Arndt.—The author has had occasion to examine alloys of calcium and aluminium containing 25, 50, and 80 per cent calcium (denoted hereafter by M_{25} , M_{50} , and M_{80} respectively). Of these, the last is by far the least brittle. The melting-points are M_{25} 765° , M_{50} 1050° , and M_{80} 600° . Although silicon was also present in the alloys from M_{80} , pure calcium could be distilled off at a red heat in vacuo, neither silicon nor aluminium coming over. When M_{50} was distilled from an iron tube the calcium coming over contained both aluminium and iron, but was quite pure when a porcelain crucible was used. Thus even large amounts of aluminium can be separated from calcium by simple distillation in a high vacuum. It is noticeable that the melting-point of M_{50} is 250° higher than that of the component (Ca 800°) of higher melting-point. Calcium-aluminium alloys may be prepared by introducing calcium into aluminium, which is fused under potassium chloride. Considerable heat is evolved, and some of the calcium burns away. They may also be prepared by electrolysis, using as cathode melted aluminium. By using an alloy of aluminium and copper as cathode, the author obtained an alloy containing aluminium, copper, calcium, and traces of silicon on electrolysis fused calcium chloride. He also succeeded in obtaining electrolytically alloys of aluminium and barium containing up to 45 per cent of barium.

Explosive Mercury Salts.—K. A. Hofmann.—The author is of the opinion that except in the case of such endothermic substances as cyanic acid and acetylene, the entrance of mercury into the molecule does not influence the energy content of the system sufficiently to render explosive decomposition possible. Chlorato-dimercuric aldehyde, $\text{C}_2\text{Hg}_2\text{ClO}_4\text{H}$, is prepared by dissolving mercuric oxide in aqueous chloric acid, adding alcoholic aldehyde, and allowing to crystallise in the cold. The crystals

explode so violently that they can only be touched very cautiously with a soft brush without suffering decomposition. It is not possible to perform a combustion for the determination of carbon, for on mixing with copper oxide the crystals explode, but from other analytical data and from their behaviour the formula is undoubtedly $C_2Hg_2ClO_4H$. Chlorato-trimercury aldehyde is prepared by adding pure acetylene to an aqueous mercuric chlorate solution. It is explosive, but far less so than the dimercure compound. If these chlorates are compared with the corresponding similarly constituted nitrate-mercury aldehydes, $NO_3Hg(Hg):C\cdot COH$ and $NO_3Hg(Hg_2O):C\cdot COH$, as regards their explosiveness, the difference in energy between chloric and nitric acids is very striking. Both nitrates can be ignited without danger, merely a slight detonation occurring, which does not injure even a thin glass vessel. Comparing the heat of formation (in water) of $HNO_3 = +48.8$ cal. and $HClO_4 = 23.9$ cal. it must be deduced that, apart from the thermic effect of the formation of calomel from the chlorates, these give up 24.9 cal. more energy than the nitrates, which explains the strikingly different activity. If acetylene is led into an aqueous mercury perchlorate solution, the white powder which separates is somewhat less sensitive to friction than the chlorate, but decomposes with about the same violence when it comes in contact with a flame. By the action of acetylene upon a mixture of mercuric nitrate solution with excess of potassium nitrite in ice-cold water containing 1 per cent of free nitric acid, a compound, $NO_2Hg(Hg):C\cdot COH$, is formed. Friction and also gentle heating cause this to decompose violently with an explosion.

No. 9, 1905.

Sulphonic Acid Anhydrides.—O. C. Billeter.—By heating benzene sulphonic chloride with silver cyanate to 140° and extracting the product with ether, large clear crystals of benzene sulphonic acid anhydride are obtained. These melt at 92° , and are soluble in chloroform, benzene, and warm ether; they deliquesce in air, forming benzene sulphonic acid, but remain unchanged in cold water for a long time, dissolving on warming. By examining quantitatively their behaviour towards water and alcohol, the author has conclusively proved that these crystals are the true anhydride, the product described by Abrahall being a decomposition product of the anhydride, i.e., the free acid. By the action of methyl sulphonic chloride on silver cyanate a substance is obtained which resembles the synthetic anhydride very closely in properties, and, like benzene sulphonic acid anhydride, gives the ethyl ester when treated with impure ether. The anhydride prepared by the action of methyl sulpho-chloride on silver methyl sulphate melts at 71° , deliquesces in the air, and is decomposed by alcohol and hot water rapidly and by cold water slowly.

Action of Sodium Polysulphide on Sodium Hydrosulphite.—A. Binz.—Sodium hydrosulphite does not react with sodium sulphide, but a vigorous reaction takes place with sodium polysulphide, H_2S and S being formed and the solution being decolourised. In presence of caustic soda definite reactions take place, and the sodium hydrosulphite takes up sulphur from the polysulphide into the sulphoxyl-complex. From quantitative experiments in which the sulphur which can be precipitated by cadmium carbonate is determined before and after the reaction, it appears that the polysulphide sulphur which enters the hydrosulphite again appears as simple sodium sulphide; hence it seems probable that a thiosulphite, $NaS\cdot SO_2Na$, is formed during the reaction, and again decomposes, forming mono-sulphide and sulphite. The action of thiosulphate upon hydrosulphite is similar to that of polysulphide, but slower. If sodium hydrosulphite and thiosulphate are allowed to stand in alkaline solution for several hours, sodium sulphide is formed. This seems to explain the appearance of sodium sulphide in originally perfectly pure alkaline hydrosulphite solutions which are not freshly made; thiosulphate

forms in them $2Na_2S_2O_4 = Na_2S_2O_3 + Na_2S_2O_5$, and then reacts as above.

Double Salts of Palladium Chloride and Bromide.—A. Gutbier.—Like platinum chloride, palladium chloride and bromide form double compounds with the halogen derivatives of organic bases. The author has prepared these double compounds with aniline and toluidine chlor- and brom-hydrate, and has found that the products result only when a small quantity of the chlor- or brom-hydrate of the organic base, dissolved in water, is allowed to act upon excess of the solution of palladium haloid. If this action is reversed, i.e., if small quantities of the palladium haloid solution are allowed to act upon excess of the aqueous solution of the organic compound, no double salts are obtained, but compounds which are derivatives of palladosamine chloride or bromide. The same products are obtained by the action of the free bases upon the palladium haloid; it appeared to be immaterial whether the base was mixed directly with the solution of palladium haloid, or whether it was employed in alcoholic solution. The author has established the identity of these products as derivatives of palladosamine, $Pd(NH_2)_2OH$; they are characterised by dissolving in ammonia, forming colourless solutions, which after boiling are precipitated by the corresponding haloid acid, giving the palladosamine chloride or bromide.

Quantitative Separation of Gold from other Metals by Hydrazine and Hydroxylamine Salts.—P. Jannasch and O. von Mayer.—Gold is precipitated quantitatively in neutral, acid, or alkaline solution by means of hydrazine. According to the temperature and the presence of certain other elements, the gold precipitate differs in character and colour, e.g., it is powdery in presence of chromium, forms spongy conglomerates in zinc solutions, &c., though not the slightest trace of the foreign metal is associated with the gold. Hydroxylamine also separates gold quantitatively in hydrochloric acid solution, but not so energetically as hydrazine, and not at a temperature below 80° . By means of hydrazine chlorhydrate gold can be separated from most metals, tin being the most notable exception; the gold precipitates always contain more or less tin.

Processes in the Reduction of Iron.—Rudolf Schenck and W. Heller.—When carbon monoxide acts at approximately atmospheric pressure on nickel and cobalt, and the changes of pressure at constant volume are observed, the reaction ceases at about half the initial pressure, i.e., when equilibrium has ensued between the two gases carbon monoxide and solid carbon. In presence of iron the case is different, the pressure at which the reaction comes to a standstill being very small. This can only occur if the metal does not act purely catalytically, but itself takes part in the reaction. Pure carbon monoxide cannot oxidise iron. Hence the authors concluded that the action consists of two processes. Firstly, the metal acts purely catalytically, causing the monoxide to be split up into dioxide and carbon until the quantity of the dioxide is increased, so that the two oxides are no longer in equilibrium with the metallic iron; then the metal is oxidised according to the equation $Fe + CO_2 = FeO + CO$, the CO being again decomposed into C and CO_2 . These two processes finally cease when perfect equilibrium has resulted between iron, iron oxide, carbon, and the two oxides. On examining the conditions for the equilibria between carbon and the two oxides, and also between iron, ferrous oxide, carbon monoxide, and carbon dioxide, it is found that a perfectly definite partial pressure and a perfectly definite total pressure of the two oxides of carbon correspond to every temperature. The knowledge of the pressure of total equilibrium is of importance in the blast-furnace process. Ferrous oxide is reduced by carbon monoxide in the presence of carbon only if the total pressure of carbon monoxide and di-oxide is less than the pressure of total equilibrium. If the pressure of the gaseous mixture is greater at the same temperature, re-oxidation of the metallic iron and separation of carbon result, which is what occurs oc-

casionally in the furnace. The authors have determined the pressures of total equilibrium for a large number of temperatures between 400° and 800° by two different methods, obtaining perfectly concordant results, and have also studied the behaviour of metallic manganese towards carbon monoxide. Manganese being much more easily oxidised than iron, it was to be expected that the pressure of total equilibrium would be much less for manganese than for pure iron. This was completely confirmed by experiment, and it was found impossible to measure the pressures at temperatures below 1200°. On the large scale, when the carbon monoxide is prepared from the air, in consequence of the presence of nitrogen the sum of the partial pressures of CO and CO₂ must not exceed one-third of an atmosphere = 250 m.m. Hence the reduction of ferrous oxide occurs at all temperatures at which the equilibrium pressure is greater than 250 m.m.; i.e., at all temperatures above 695°. If manganese is present in the iron the limit of reduction lies much higher than 695°.

Relations of the Different Modifications of Carbon to one another.—Rudolf Schenck and W. Heller.—Since at high temperatures both amorphous carbon and the diamond pass into graphite, the last is regarded as the most stable of the carbon modifications. The different modifications undoubtedly possess different amounts of free energy, and hence the constants of equilibrium between CO, CO₂, and the different forms of solid carbon must possess different values at the same temperature, being greatest for the most labile form and least for the most stable. If the total pressure of the two gases is denoted by P, the equilibrium constant of the carbon equilibrium (C, CO, CO₂) by ζ, and that of the system Fe, FeO, CO, CO₂ by η; then $P = \zeta \cdot \frac{1 + \eta}{\eta}$, whence

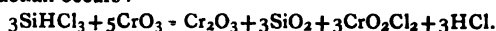
the values of ζ for the different carbon modifications are directly proportional to the pressures of total equilibrium (at constant temperature). The authors determined the values of ζ for the different modifications for temperatures ranging from 400—800°, and on representing these graphically they found that the temperature-pressure curves differed considerably. Amorphous sugar carbon showed the highest pressure, and is the most labile form, while graphite is the most stable. Comparing the carbon prepared from carbon monoxide with graphite they obtained the same curve, whence they concluded that this carbon is merely very finely divided graphite. The curve for the diamond is intermediate between that for graphite and amorphous carbon, being nearer the latter. The diamond is thus a meta stable form of carbon.

Determination of Sugar with Fehling Solution.—F. P. Lavalle.—Already noticed.

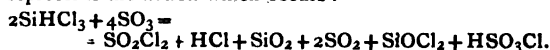
Colloid Copper Oxide.—H. Ley.—For preparing colloid oxide of copper a salt has to be used which contains a very feeble acid constituent. Copper succinimide is well suited for this purpose. This salt is prepared by the action of a copper-mercury amalgam on mercury succinimide. The aqueous solution of this salt, on being allowed to stand for some days, gradually changes in colour from blue-green to brown. On the addition of electrolytes, such as the chlorides and nitrates of potassium and barium, a brown flocculent copper oxide appears, which may be separated from the unchanged succinimide by dialysis. Hence the brown solution contains the copper oxide in the colloid condition. Like most other metallic hydroxide colloids, it is positive, and migrates to the cathode.

Silico-chloroform.—Otto Ruff and Kurt Albert.—The authors could not succeed in discovering any new method of preparing silico-chloroform, but they have investigated the properties of the compound, using a purified specimen prepared in the usual way. The boiling-point they found to be 33° and melting-point -134° absolute; the density at 15° = 1.3438. When led through a heated glass tube the compound is decomposed according to the equation $4\text{SiHCl}_3 \rightleftharpoons \text{Si} + 3\text{SiCl}_4 + 2\text{H}_2$, which is reversible at 800°.

Silico-chloroform does not react with metals, aluminium chloride, sulphur, and red phosphorus. It possesses the power of reducing oxides, e.g., with CrO₃ the following reaction occurs:—



With sulphur trioxide the following equation apparently represents the action which occurs:—



Arsenious and antimonious oxides are both reduced to the metal when SiHCl₃ acts upon them in alkaline solution. With ammonia the following action takes place:— $\text{SiHCl}_3 + 4\text{NH}_3 = \text{SiNH} + 3\text{NH}_4\text{Cl}$. The silicon nitrogen hydride is very readily decomposed, and hence its investigation presents many difficulties, but the authors have succeeded in proving that it is a derivative of tetravalent silicon; apparently the tetravalent silicon in silico-chloroform and its derivatives never passes into trivalent silicon, splitting off H, and forming silicon hexachloride, for instance.

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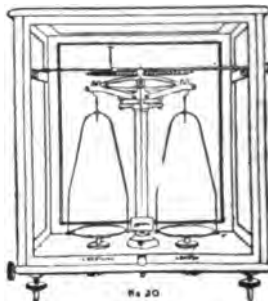
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ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. SOUTH AFRICA, 1905.

By G. T. BEILBY, President of the Section.

IN scanning the list of the elements with which we are thoughtfully supplied every year by the International Committee on Atomic Weights, the direction in which our thoughts are led will depend on the particular aspect of chemical study which happens to interest us at the time. Putting from our minds on the present occasion the attractive speculations on atomic constitution and disintegration with which we have all become at least superficially familiar during the past few years, let us try to scan this list from the point of view of the "plain man" rather than from that of the expert chemist. Even a rudimentary knowledge will be sufficient to enable our "plain man" to divide the elements broadly into two groups—the actually useful and the doubtfully useful or useless. Without going into detail we may take it that about two-thirds would be admitted into the first group, and one-third into the second. It must, I think, be regarded as a very remarkable fact that of the eighty elements which have had the intrinsic stability to enable them to survive the prodigious forces which must have been concerned in the evolution of the physical universe, so large a proportion are endowed with characteristic properties which could ill have been spared either from the laboratories of Nature or from those of the Arts and Sciences. Even if one-third of the elements are to be regarded as waste products or failures, there is here no counterpart to the reckless prodigality of Nature in the processes of organic evolution.

If we exclude those elements which participate directly and indirectly in the structure and functions of the organic world, there are two elements which stand out conspicuously because of the supreme influence they have exercised over the trend of human effort and ambition. I refer, of course, to the metals gold and iron.

From the early beginnings of civilisation gold has been highly prized and eagerly sought after. Human life has been freely sacrificed in its acquirement from natural sources, as well as in its forcible seizure from those who already possessed it. The "Age of Gold" was not necessarily "The Golden Age," for the noble metal in its unique and barbaric splendour has symbolised much that has been unworthy in national and individual aims and ideals.

We have accustomed ourselves to think of the present as the Age of Iron, as indeed it is, for we see in the dull grey metal the plastic medium out of which the engineer has modelled the machines and structures which play so large a part in the active life of to-day. Had iron not been at once plentiful and cheap, had it not brought into the hands of the engineer and artificer its marvellous qualities of hardness and softness, of rigidity and toughness, and to the electrician its mysterious and unique magnetic qualities, it is not difficult to conceive that man's control over the forces of Nature might have been delayed for centuries, or perhaps for ages. For iron has been man's chief material instrument in the conquest of Nature; without it the energy alike of the waterfall and of the coalfield would have remained uncontrolled and unused. In this conquest of the resources of Nature for the service of man are we not entitled to say that the intellectual and social gains have equalled, if they have not exceeded, in value the purely

material gains; and may we not then regard iron as the symbol of a beneficent conquest of Nature?

With the advent of the Industrial Age gold was destined to take a new place in the world's history as the great medium of exchange, the great promoter of industry and commerce. While individual gain still remained the propelling power towards its discovery and acquisition, every fresh discovery led directly or indirectly to the freer interchange of the products of industry, and thus reacted favourably on the industrial and social conditions of the time.

So long as the chief supplies of gold were obtained from alluvial deposits by the simple process of washing, the winning of gold almost necessarily continued to be pursued by individuals, or by small groups of workers, who were mainly attracted by the highly speculative nature of the occupation. These workers endured the greatest hardships and ran the most serious personal risks, drawn on from day to day by the hope that some special stroke of good fortune would be theirs. This condition prevailed also in fields in which the reef gold occurred near the surface, where it was easily accessible without costly mining appliances, and where the precious metal was loosely associated with a weathered matrix. These free-milling ores could be readily handled by crushing and amalgamation with mercury, so that here also no elaborate organisation and no great expenditure of capital were necessary. A third stage was reached when the more easily worked deposits above the water-line had been worked out. Not only were more costly appliances and more elaborately organised efforts required to bring the ore to the surface, but the ore when obtained contained less of its gold in the easily recovered, and more in the refractory or combined form. The problem of recovery had now to be attacked by improved mechanical and chemical methods. The sulphides or tellurides with which the gold was associated or combined had to be reduced to a state of minute sub-division by more perfect stamping or grinding, and elaborate precautions were necessary to ensure metallic contact between the particles of gold and the solvent mercury. In many cases the amalgamation process failed to extract more than a very moderate proportion of the gold, and the quartz sand or "tailings" which still contained the remainder found its way into creeks and rivers or remained in heaps on the ground around the batteries. In neighbourhoods where fuel was available a preliminary roasting of the ore was resorted to, to oxidise or volatilise the baser metals and set free the gold; or the sulphides, tellurides, &c., were concentrated by washing, and the concentrates were taken to smelting or chlorinating works in some favourable situation where the more elaborate metallurgical methods could be economically applied. Many efforts were also made to apply the solvent action of chlorine directly to the unconcentrated unroasted ores; but unfortunately chlorine is an excellent solvent for other substances besides gold, and in practice it was found that its solvent energy was mainly exercised on the base metals and metalloids, and on the materials of which the apparatus itself was constructed.

This to the best of my knowledge is a correct, if rather sketchy, description of the state of matters in 1889 when the use of a dilute solution of cyanide of potassium was first seriously proposed for the extraction of gold from its ores. Those of us who can recall the time will remember that the proposal was far from favourably regarded from a chemical point of view. The cost of the reagent, its extremely poisonous nature, the instability of its solutions, its slow action—such were the difficulties that naturally presented themselves to our minds. And, even granting that these difficulties might be overcome, there still remained the serious problem of how to recover the gold in metallic form from the extremely dilute solutions of the cyanide of gold and potassium. How each and all of these difficulties have been swept aside, how within little more than a decade this method of gold extraction has spread over the gold-producing countries of the world, now

absorbing and now replacing the older processes, but ever carrying all before it—all this is already a twice-told tale which I should feel hardly justified in alluding to were it not for the fact that we are to-day meeting on the Rand where the infant process made its début nearly fourteen years ago. The Rand to-day is the richest of the world's goldfields, not only in its present capacity, but in its potentialities for the future; twenty years ago its wonderful possibilities were quite unsuspected even by experts.

It is not for me to describe in detail how the change has been accomplished; this task will, we know, be far better accomplished by representative chemists who are now actively engaged in the work. But for the chemists of the British Association it is a fact of great significance that they are here in the presence of the most truly industrial development of gold production which the world has yet seen; a development, moreover, that is founded on a purely chemical process which for its continuance requires, not only skilled chemists to superintend its operation, but equally skilled chemists to supply the reagent on which the industry depends.

In 1889, the world's consumption of cyanide of potassium did not exceed fifty tons per annum. This was produced by melting ferrocyanide with carbonate of potassium, the clear fused cyanide so obtained being decanted from the carbide of iron which had separated. The resulting salt was a mixture of cyanide, cyanate, and carbonate which was sometimes called cyanide of potassium for the hardly sufficient reason that it contained 30 per cent of that salt. When the demand for gold extraction arose, it was at first entirely met by this process, the requisite ferrocyanide being obtained by the old fusion process from the nitrogen of horns, leather, &c. In 1891, the first successful process for the synthetic production of cyanide without the intervention of ferrocyanide was perfected, and the increasing demand from the gold mines was largely met by its use. At present the entire consumption of cyanide is not much short of 10,000 tons a year, of which the Transvaal gold-field consumes about one-third. Large cyanide works exist in Great Britain, Germany, France, and America, so that a steady and sure supply of the reagent has been amply provided. In 1894, the price of cyanide in the Transvaal was 2s. per pound; to-day it is one-third of that, or 8d. During the prevalence of the high prices of earlier years the manufacture was a highly speculative one, and new processes appeared and disappeared with surprising suddenness, the disappearance being generally marked by the simultaneous vanishing of large sums of money. To-day the manufacture is entirely carried out in large works scientifically organised and supervised, and, both industrially and commercially, the speculative element has been eliminated.

Chemistry has so often been called on to play the part of the humble and unrecognised handmaiden to the industrial arts that we may perhaps be pardoned if in this case we call public attention to our Cinderella as she shines in her rightful position as the genius of industrial initiation and direction.

To this essentially chemical development of metallurgy we owe it that in a community whose age can only be counted by decades we find ourselves surrounded by chemists of high scientific skill and attainments who have already organised for their mutual aid and scientific enlightenment "The Johannesburg Society of Chemistry, Metallurgy, and Mining," whose published proceedings amply testify to the atmosphere of intellectual vigour in which the work of this great industry is carried on.

It appears, then, that while gold still maintains its position of influence in the affairs of men, the nature of that influence has undergone an important change. Not only has its widespread use as the chief medium of exchange exercised far-reaching effects on the commerce of the world, but the vastly increased demand for this purpose has in its turn altered the methods of production. These methods have become more highly organised and scientific, and gold production is now fairly established as a progres-

sive industry in which scope is found for the best chemical and engineering skill and talent.

The experience of more highly evolved industries in the older countries has shown that the truly scientific organisation of industry includes in its scope a full and just consideration for the social and intellectual needs of its workers from highest to lowest. It augurs well, therefore, for the future of the gold industry, from the humane and social points of view, that its control should be more and more under the influence of men of scientific spirit and intellectual culture who we may feel assured will not forget the best traditions of their class.

The application of science to industry requires on the part of the pioneers and organisers keen and persistent concentration on certain well-defined aims. Any wavering in these aims or any relaxation of this concentration may lead to failure or to only a qualified success. This necessary but narrow concentration may be a danger to the intellectual development of the worker, who may thereby readily fall into a groove, and so may become even less efficient in his own particular work. It certainly requires some mental strength to hold fast to the well-defined practical aim while allowing to the attention occasional intervals of liberty to browse over the wide and pleasant fields of science. But I am certain that the acquirement of this double power is well worth an effort. The mental stimulus, as well as the new experiences garnered during the excursion, will sooner or later react favourably on the practical problems, while the earnest wrestling with these problems may develop powers and intuitions which will lend their own charm to the wider problems of science.

Gold and Science.

If we re-peruse the table of the elements, not now in our capacity as "plain men" but as chemists, we shall certainly not select gold as of supreme interest chemically. Its position as chief among the noble metals, its patent of nobility, is based on its aloofness from common associations or attachments. Unlike the element nitrogen, it is mainly for itself, and little if at all for its compounds, that gold is interesting. In it we can at our leisure study the *metal* rather than the *element*. Its colour and transparency, its softness and its hardness, the density as well as the extreme tenuity of some of its forms—such were the qualities which recommended it to Faraday when he desired to study the action of material particles on light. I should like to repeat to you in his own words the reasons he gave for this choice:—"Because of its comparative opacity among bodies, and yet possession of a real transparency; because of its development of colour both in the reflected and transmitted rays; because of the state of tenuity and division which it permitted with the preservation of its integrity as a metallic body; because of its supposed simplicity of character; and because known phenomena appeared to indicate that a mere variation in the size of its particles gave rise to a variety of resultant colours. Besides the waves of light are so large compared to the dimensions of the particles of gold which in various conditions can be subjected to a ray, that it seemed probable that the particles might come into effective relations to the much smaller vibrations of the other particles."

I may remind you that Faraday came to the conclusion that the variety in the colours presented by gold under various conditions is due to the size of its particles and their state of aggregation. Ruby glass or ruby solutions he proved are not true solutions, nor are they molecular diffusions of gold, but they contain the metal in aggregates sufficiently large to give a sensible reflection under an incident beam of light. Through the kindness of Sir Henry Roscoe I am able to exhibit to you some of the original ruby gold preparations obtained during this research, which were afterwards presented to him by Faraday at the Royal Institution some years before his death.

By means of refined and ingenious optical methods,

Zigsmundy and Siedentopf have succeeded in making these ultra-microscopic particles visible in the microscope as diffraction discs; they have, further, counted the number of particles per unit area, and have from the intensity of their reflection calculated their size. In ruby glass the size of the particles in different specimens was found to vary from 4 to 791 millionths of a millimetre. No relation was found to hold between the colour of the particles and their absolute size. This conclusion is in direct contradiction of Faraday's belief already referred to. Mr. J. Maxwell Garnett has recently shown that the colour of metallic glasses and films is determined, not only by the absolute size of the metal particles, but also by the proportion of the total volume they occupy in the medium in which they are diffused. The results of Mr. Garnett's calculations are in close agreement with a number of the observations on the colour and micro-structure of thin metal films which I had already recorded, and they appear to me to supply the explanation of much that had appeared puzzling before. My own observations lead me to think that the actual microscopic particles which are to be seen, and the larger of which can also be measured, in films and solutions or suspensions, do not in any way represent the ultimate units of structure which are required by Mr. Garnett's theory, but that these particles are aggregates of smaller units built up in more or less open formation.

That a relatively opaque substance like gold may be so attenuated that when disseminated in open formation it becomes transparent, is contrary to all our associations with the same operation when performed on transparent substances like glass or crystalline salts. The familiar experiment of crushing a transparent crystal into a perfectly opaque powder would not prepare us for the effect of minute sub-division on the transparency of metals. At first it might be supposed that this difference is due to the very rough and incomplete sub-division of the crystal by crushing; but this is not the case, for the perfectly transparent oxide of magnesium may be obtained in a state of attenuation comparable with that of the gold, by allowing the smoke from burning magnesium to deposit on a glass plate. The film of oxide obtained in this way is found to be built up of particles quite as minute as those of which the gold films are composed, yet the opacity of the oxide film is relatively much greater. The minute particles of the dielectric, magnesium oxide, scatter and dissipate the light waves by repeated reflection and refraction, while the similar particles of the metallic conductor, gold, act as electrical resonators which pass on some of the light waves while reflecting others. Specimens of films of gold and silver and of magnesium oxide are exhibited on the table and on the lantern screen. When the metallic particles are in this state of open formation and relative transparency, it was found that the electrical conductivity of the films had completely disappeared. Films of this description were found to have a resistance of over 1,000,000 megohms as compared with only six ohms in the metallic reflecting condition.

Molecules in the Solid State.

My examination of gold films and surfaces has revealed the fact that during polishing the disturbed surface film behaves exactly like a liquid under the influence of surface tension. At temperatures far below the melting-point molecular movement takes place under mechanical disturbance, and the molecules tend to heap up in minute mounds or flattened droplets. These minute mounds are often so shallow that they can only be detected when the surface is illuminated by an intense, obliquely incident beam of light. I have estimated that these minute mounds or spicules can be seen in this way in films which are not more than five to ten micro-millimetres in thickness. A film of this attenuation may contain so few as ten to twenty molecules in its thickness.

When moderately thin films of gold are supported on glass, and heated at a temperature of 400–500°, they become translucent, and the forms assumed under the influence of surface tension can be readily seen by trans-

mitted light. It was in this way that the beautiful but puzzling spicular appearance by obliquely reflected light was first explained as due to the granulation of the surface under the influence of surface tension. Photo-micrographs of these films are exhibited.

Turning now to the mechanical properties of metals, we find that gold has proved itself of great value in the investigation of some of these. It has long been recognised as the most malleable and ductile of the metals, whilst its chemical indifference tends to preserve it in a state of metallic purity throughout any prolonged series of operations.

The artificers in gold must very early have learned that its malleability and ductility are not qualities which indefinitely survive the operations of hammering and wire-drawing. A piece of soft gold beaten into a thin plate does not remain equally soft throughout the process, but spreads with increasing difficulty under the hammer. If carelessly beaten it may even develop cracks round its edges. We may assume that the artificers in gold very soon discovered that by heating, the hardened metal might be restored to its former condition of softness.

In connection with the study of the micro-metallurgy of iron and steel during recent years it has been recognised that heat annealing is, as a rule, associated with the growth and development of crystalline grains, and Professor Ewing and Mr. Rosenhain have shown that overstrain is often if not invariably associated with the deformation of these crystalline grains by slips occurring along one or more cleavage planes. This hypothesis, though well supported up to a point by microscopic observations on a variety of metals, offers no explanation of the natural arrest of malleability or ductility which occurs when the overstrain has reached a point at which the crystalline grains are still, to all appearance only, slightly deformed. At this stage there is no obvious reason why the slipping of the crystalline lamellæ should not continue under the stresses which have initiated it. But far from this being the case, a relatively great increase of stress produces little or no further yielding till the breaking point is reached and rupture takes place.

The study of the surface effects of polishing, already referred to, had shown that the thin surface film retained no trace of crystalline structure; while it also gave the clearest indications that the metal had passed through a liquid condition before settling into the forms prescribed by surface tension. From this it was argued that the conditions which prevail at the outer surface might equally prevail at all inner surfaces where movement had occurred, so that every slip of one crystalline lamella over another would cause a thin film of the metal to pass through the liquid phase to a new and non-crystalline condition. By observations on the effects of beating pure gold foil, it was found that the metal reached its hardest and least plastic condition only when all outward traces of crystalline structure had disappeared. It was also ascertained that this complete destruction of the crystalline lamellæ and units could only be accomplished in the layers near the surface, for the hardened substance produced by the flowing under the hammer appears to encase and protect the crystalline units after they become broken down to a certain size. By carefully etching the surface in stages by means of chlorine water or cold aqua regia, the successive layers below the surface were disclosed. The surface itself was vitreous; beneath this was a layer of minute granules, and lower still the distorted and broken-up remains of crystalline lamellæ and grains were embedded in a vitreous and granular matrix. The vitreous-looking surface layer represents the final stage in the passage from soft to hard, from crystalline to amorphous. By heating the beaten foil, its softness was restored; and on etching the annealed metal it was found that the crystalline structure also was fully restored. Photomicrographs showing these appearances are exhibited. These microscopic observations were fully confirmed by finding well-marked thermo-electrical and electro-chemical distinctions

between the two forms of metal, the hard and soft or the amorphous and the crystalline. The determination of a definite transition temperature at which the amorphous metal passes into the crystalline metal further confirms the phase view of hardening by overstrain and softening by annealing.

It was subsequently proved that *the property of passing from crystalline to amorphous by mechanical flow, and from amorphous to crystalline by heat at a definite transition temperature, is a general one which is possessed by all crystalline solids which do not decompose at or below their transition temperature.* The significance of this fact I venture to think entitles it to more than a passing reference. It appears to me to mean that the transition from amorphous to crystalline is entitled to take its place with the other great changes of state, solid to liquid, liquid to gas, for like these it marks a change in the molecular activity which occurs when a certain temperature is reached. It is entitled to take this place because there is every indication that the change is as general in its nature as the other changes of state. Compare it, for instance, with the allotropic changes with which chemists have been familiar. These are for the most part changes which are special to particular elements or compounds, and are usually classed with the chemical properties by which the substances may be distinguished from each other. Very different is the amorphous crystalline change, for although in particular cases it may have been observed and associated with allotropic changes, yet the causes of its occurrence are more deeply founded in the relations between the molecules and the heat energy by which their manifold properties are successively unfolded as temperature is raised from the absolute zero. At this transition-point we find ourselves face to face with the first stirrings of a specific directive force by which the blind cohesion of the molecules is ordered and directed to the building up of the most perfect geometric forms. It is hardly possible any longer to regard the stability of a crystal as static and inert, and independent of temperature; rather must its structure and symmetry be taken as the outward manifestation of a dynamic equilibrium between the primitive cohesion and the kinetic energy imparted by heat. Even before the discovery of a definite temperature of transition from the amorphous to the crystalline phase we had in our hands the proofs that in certain cases the crystalline state can be a state of dynamic, rather than of static equilibrium. The transition of sulphur from the rhombic to the prismatic form supplies an example of crystalline stability which persists only between certain narrow limits of temperature. Within these limits the crystal is a "living crystal" if one may borrow an analogy from the organic world. It can still grow, and it will under proper conditions repair any damage it may receive.

The passage of the same substance through several crystalline phases, each only stable over a limited range of temperature, strongly supports the general conclusion drawn from the existence of a stability temperature between the amorphous and crystalline phases, namely, that the crystalline arrangement of the molecules requires for its active existence the particular kind or rate of vibration corresponding with a certain range of temperature. Below this point the crystal may become to all appearance a mere pseudomorph with no powers of active growth or repair. But these powers are not extinct—they are only in abeyance ready to be called forth under the energising influence of heat. This temporary abeyance of the more active properties of matter is strikingly illustrated by the early observations of Sir James Dewar at the boiling-point of liquid air, and more recently at that of liquid hydrogen. At the latter temperature even chemical affinity becomes latent. In metals it was found that the changes in their physical properties brought about by these low temperatures are not permanent, but only persist so long as the low temperature is maintained. During the past year Mr. R. A. Hadfield has supplemented these earlier results by making a very complete series of observations on the effect

of cooling on the mechanical properties of iron and its alloys. The tenacity and hardness of the pure metal and its alloys at the ordinary temperature and at -182° have been compared, and it has been found that these qualities are invariably enhanced at the lower temperature, but that they return exactly to their former value at the ordinary temperature. By the mere abstraction of heat between the temperatures of 18° and -182° the tensile strength of pure metals is raised 50 to 100 per cent. In pure iron the increase is from 23 tons per square inch at 18° C. to 52 tons at -182° ; in gold from 15.1 tons to 22.4 tons; and in copper from 19.5 tons to 26.4. This increase is not, I think, due to the closer approximation of the molecules, for the coefficient of expansion of most metals below 0° is extremely small. Neither is it due to permanent changes of molecular arrangement or aggregation, for Mr. Hadfield has obtained a perfectly smooth and regular cooling curve for iron between 18° and -182° , and there appears to be no indication of the existence of any critical point between these temperatures. Further, the complete restoration of the original tenacity on the return to the higher temperature shows that no permanent or irreversible change has occurred during cooling. Everything therefore indicates that the increase of tenacity which occurs degree by degree as heat is removed is due to the reduction of the repulsive force of molecular vibration, so that the primary cohesive force can assert itself more and more completely as the absolute zero is approached.

The metals experimented with by Mr. Hadfield were all in the annealed or crystalline condition, so that the molecules must have exerted their mutual attractions along the directed axes proper to this state. It is to be expected that similar experiments with the metals in the amorphous state may throw light on the question whether and to what extent the crystalline state depends on a dynamic equilibrium between the forces of cohesion and repulsion, or whether a directed cohesion exists fully developed in the molecules at the absolute zero.*

The phenomena of the solid state throw an interesting light on the interplay of the two great forces, the primitive or blind cohesion which holds undisputed sway at the absolute zero, and the repulsion due to the molecular vibrations which is developed by heat. This interplay we know continues through the states which succeed each other as the temperature is raised, till a point is reached at which the molecular repulsions so far outweigh the cohesive force that the substance behaves like a perfect gas. The problems of molecular constitution are more likely to be elucidated by a study of the successive states between the absolute zero and the vaporising temperature than at the upper ranges where the gaseous state alone prevails. The simplicity of the laws which govern the physical behaviour of a perfect gas is very attractive, but we must not forget that this simplicity is only possible because repulsion has so nearly overcome cohesion that the latter may be practically ignored. The attractiveness of this simplicity should not blind us to the fact that it is in the middle region, where the opposing forces are more nearly equal, that the most interesting and illuminating phenomena are likely to abound. The application of the gas laws to the phenomena of solution and osmosis appears to be one of those cases in which an attractive appearance of simplicity in the apparent relations may prove very misleading.

Before passing from the specially metallic qualities of gold I will only remind you of the important part it has played in the researches on the diffusion of metals by the late Sir William Roberts-Austen, and in those of Mr. Haycock and Mr. Neville on the freezing-points of solutions of gold in tin, which led to the recognition of the monatomic nature of the molecules of metals.

* Since the above was written a series of observations has been made on the influence of low temperature on the tenacity of pure metals in the amorphous condition. These observations will form the subject of a separate communication to the Section.

Molecules in Solution.

It has occurred to me that the practice of the cyanide process of gold extraction presents us with several new and interesting aspects of the problems of solution. As you are aware, the gold is first obtained from the ore in the form of a very dilute solution of cyanide of gold and potassium from which the metal has to be separated, either by passing it through boxes filled with zinc shavings, or by electrolysis in large cells.

The solution as it leaves the cyanide-vats may contain gold equal to 100 grains or more per ton, and as it leaves the precipitating-boxes it may contain as little as 1 or 2 grains and as much as 20 grains. In the treatment of slimes much larger volumes of solution have to be dealt with, and in this case solutions containing 18 grains per ton have been regularly passed through the precipitating-boxes, their gold content being reduced to $1\frac{1}{2}$ grains per ton. In round numbers we may say that 1 grm. of gold is recovered from 1 cubic metre of solution, while 0.1 grm. is left in the solution. Even from the point of view of the physical chemist we are here in presence of solutions of a very remarkable order of dilution. A solution containing 1 grm. per cubic metre is in round numbers $N/200,000$, and the weaker solution containing 0.1 grm. is $N/2,000,000$. It is convenient to remember that the latter contains a little more than $1\frac{1}{2}$ grains per ton. In experiments on the properties of dilute solutions the extreme point of dilution was reached by Kohlrausch, who employed solutions containing $1/100,000$ of a grm. molecule of solute per litre for his conductivity experiments. These solutions were therefore twice as strong as the gold solution with 1 grm. per cubic metre, and twenty times as strong as the more dilute solution. This fact must be my excuse for placing before you the results of a few simple calculations as to the molecular distribution in these solutions, which have certainly given me an entirely new view of what constitutes a really dilute solution from the molecular point of view.

In estimating the number of molecules in a given volume of solution the method adopted is to divide the space into minute cubical cells, each of which can exactly contain a sphere of the diameter of the molecule. In this way a form of piling for the molecules is assumed which, though not the closest possible, may quite probably represent the piling of water molecules. Taking the molecular diameter as 0.2×10^{-8} millimetres—a figure which is possibly too small for the water molecules and too large for the gold—it is found that a cubic millimetre of solution contains 125×10^{18} molecules, or 125 quadrillions. The head of an ordinary pin, if it were spherical, would have a volume of about 1 cubic millimetre.

If these water molecules could be arranged in a single row, each molecule just touching its two nearest neighbours, the length of the row would be 25,000,000 kilometres. A thread of these fairy beads, which contained the molecules of one very small drop of a volume of 6 cubic millimetres, would reach from the earth to the sun, a distance of about 150,000,000 kilometres.

In a solution containing $1\frac{1}{2}$ grains of gold per ton, or 1 decigram. per cubic metre, the ratio of gold molecules to water molecules is as 1 : 193,000,000. Each cubic millimetre of the solution therefore contains 6,500,000,000 gold molecules. If these are uniformly distributed throughout the solution each will be about 400 micro-millimetres, or $1/60,000$ of an inch, from its nearest neighbours. This is not really very wide spacing, for the point of the finest sewing-needle would cover about 1500 gold molecules.

If a cubic metre of solution could be spread out in a sheet one molecule in thickness it would cover an area of 1680 square miles, and nowhere in this area would it be possible to put down the point of the needle without touching some hundreds of gold molecules simultaneously.

According to Professor Liversidge, sea-water contains on the average about 1 grain of gold per ton. If this is the case, then the above figures for the dilute cyanide solution apply with only a slight modification to sea-water. No drop, however small it may be, can be removed from the

ocean which will not contain many millions of gold molecules, and no point of its surface can be touched which is not thickly strewn with these. From this molecular point of view we must realise that our ships literally float on a gilded ocean!

From time to time adventurers arise who attempt to launch upon this gilded ocean unseaworthy ships freighted with the savings of the trusting investor. In order that nothing which has been said here may tempt anyone to contribute to the freighting of these ships, let me hasten to point out that the weakest of the cyanide solutions here referred to is richer in gold than sea-water is reported to be. The practical conclusion from this comparison is sufficiently obvious. If the cyaniding expert, whose business it is to extract gold from dilute solutions, finds that it does not pay to carry this extraction beyond a concentration of 2 or 3 grains per ton, even when the solution is already in his hand, and when therefore the costs of treatment are at their minimum, how can it possibly pay to begin the work of extraction on sea-water, a solution of one-half the richness, which would have to be impounded and treated by methods which could not fail to be more costly in labour and materials than the simple process of zinc-box precipitation? It is generally unsafe to prophesy, but in this case I am rash enough to risk the prediction that if ever the gold mines of the Transvaal are shut up it will *not* be owing to the competition of the gold resources of the ocean.

In these calculations with reference to the dilute cyanide solutions it is assumed that the gold molecules are uniformly distributed, that they are practically equidistant from each other. There appears to me to be considerable doubt whether we have any right to make this assumption. Leaving out of account for the moment the action of the water molecules, it would appear that as long as the gold molecules are so numerous that a uniform distribution would bring them within the range of each other's attraction, we can imagine that all submerged molecules would be in equilibrium so far as the attractions of their own kind are concerned, being subjected to a uniform pull in all directions. This condition would certainly make for uniform distribution. But when the distance between them exceeds the range of the molecular forces, it is evident that an entirely new condition is introduced, and it seems not improbable that the widely distributed molecules would tend to drift into clouds in which they are brought back within the range of these forces. The range of the cohesive forces in water and aqueous liquids is usually taken from 50 to 100 micro-millimetres, and I am disposed to think that ten times this amount would not be an excessive estimate of the range in the case of gold. If the range for gold be taken as 500 micro-millimetres, then the gold molecules of the dilute gold solution, which are spaced at 400 micro-millimetres apart, are just within the range of each other's attraction, and their distribution is therefore likely to be uniform. But by a further dilution to half concentration, the equilibrium would be liable to be disturbed, and denser clouds of gold molecules would be formed, with less dense intervals between them.

In preparing the zinc boxes through which the gold solution is passed, very great care has to be exercised to ensure that the contact surface of the zinc is used to the best advantage. With this object the packing of the zinc shavings is so managed that the solution is spread over the zinc surface in as thin sheets as possible. The object, of course, is to bring as many of the gold molecules as possible into actual contact with the zinc. The gold molecules found in the solution leaving the boxes are those which have not been in contact with the zinc. Yet we have seen that these molecules are still so numerous that they are within $1/60,000$ of an inch of each other. If these molecules are in a state analogous to the gaseous state, with diffusive energy of the same order as that of the gas molecule, it is difficult to imagine how they can escape without coming in contact with the zinc surface during their tortuous passage through the boxes and being deposited there. Yet they do escape, even when the

velocity of the solution in passing over the zinc surfaces is so slow as 10 c.m. per minute, or 1.6 m.m. per second.

We may regard the condition of these isolated gold molecules, or the more complex auricyanide of potassium molecules, as typical of that of the solute molecules in a dilute solution of any non-volatile solid. They are *solid* molecules sparsely distributed among a multitude of intensely active solvent molecules, the temperature of the solution being many hundred degrees below that at which they could of themselves assume the greater freedom of the liquid or gaseous state. These solute molecules have to a great extent been set free from the constraining effect of their cohesive forces, *but it is important to remember that this freedom has not been attained by the increase of their own kinetic energy as in liquefaction by heat.* Their freedom and the extra kinetic energy they have acquired have in some way been imparted to them by the more active solvent molecules; for, if the solvent could be suddenly removed, leaving the solute molecules still similarly distributed in a vacuous space, they would eventually condense into a solid aggregate. This must be the case, for the non-volatile solute has no measurable vapour pressure at the temperature of the solution. The kinetic energy of the solute molecules is of itself quite insufficient to endow them with the properties of the gaseous or even of the liquid molecule, even when their cohesive forces have been weakened or overcome by separation.

If the energy employed in this separation is not intrinsic to the solute molecule then it must in some way have been imparted by the solvent molecules. It therefore becomes important to compare the energy endowment of one set of molecules with that of the other.

Compared with other solids, ice at its freezing-point has very little hardness or tenacity; the cohesion of its molecules has been much relaxed by the great absorption of heat energy between the absolute zero and the freezing-point. If an average specific heat of 0.5 over the whole range be assumed, the heat absorption of 1 grm. amounts to 136.5 calories. In the transition to the liquid state at 0° a further absorption of 79 calories takes place, so that a grm. of liquid water at the freezing-point contains the heat energy of 215.5 calories. The fact that water has the high vapour pressure of 4.6 m.m. of mercury at the freezing-point is probably a result of this enormous store of energy. As a liquid, therefore, it is natural to expect that its molecules will exhibit effects proportionate to this great store of energy. This expectation appears to be realised when we consider, not only its properties as the universal solvent, but its osmotic and diffusive energy in solutions in which it is the solvent.

To complete the comparison it is only necessary to calculate the heat energy of gold at 0°. Taking its specific heat as 0.032, a grm. of gold at 0° contains 8.7 calories. A grm.-molecule, therefore, contains in round numbers 1700 calories, as compared with 3880 calories in a grm.-molecule of water.

Taking into consideration not only this greater store of energy, but also the much smaller cohesive force of water as compared with the majority of solid solutes, there can be no doubt that the active rôle in aqueous solutions of this type must be assigned to the solvent, not to the solute molecules.

This leads to the important conclusion that the energy of solution, of diffusion, and of osmosis is due, not to the imaginary gaseous energy of the solute, but to the actual liquid energy of the solvent molecules. When this conclusion is reached a new physical explanation of these phenomena is in our hands, and we are relieved from the strain to the imagination involved in the application of the gas theory to solutions of non-volatile solids.

This transference of the active rôle to the solvent molecules does not in any way affect the well-established conclusions based on the laws of thermodynamics as to the energy relations in these phenomena, for it has always been recognised that these conclusions have reference to the average conditions prevailing in large collections of

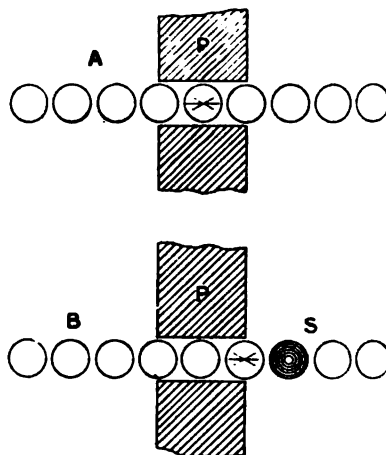
relatively minute units. Wherever the gas analogy has appeared to hold it has not necessarily involved more than this, that the observed effects are in proportion to the number of these minute units in a given volume.

In applying the gas theory to the physical explanation of osmotic pressure, it has been the custom to regard this pressure as directly due to the bombardment of the semi-permeable membrane by the solute molecules. But this conception completely ignores the fact that the pressure developed is a hydrostatic—not a gaseous—pressure, and that the hydrostatic pressure results directly from the *penetration of the solvent molecules from the other side of the partition.*

It appears to me more natural to abandon the gas analogy altogether, to regard the molecules as in the solid and liquid condition proper to their temperature, and to apportion to them their respective parts in the active changes according to their obvious endowment of energy.

Applying this view to the case of a solution and a solvent separated by a semi-permeable membrane, it is seen that the pressure rises on the solution side, because the pure solvent molecules on the other side have some advantage for the display of their energy over the similar molecules in the solution. *This effect, in its most general form, may be attributed to the dilution of the solvent by the solute molecules.* In cases where the osmotic pressure appears to obey Boyle's law, the effect is exactly measured by the number of solute molecules per unit volume. But the facts of this position are in no way changed if the effect is taken to be due to the activity of an equal number of solvent molecules, for we then see that each solute molecule, by cancelling the activity of one solvent molecule on the solution side, permits a solvent molecule from the other side to enter the solution.

What the exact mechanism of this cancellation is there is at present no evidence to show, and the caution originally given by Lord Kelvin with reference to the undue forcing of the gas analogy must also be applied to the suggestion now put forward. But as a means of making the suggestion a little more clear I give here a simple diagram



on which A represents a single perforation in a semi-permeable membrane, P, on both sides of which there is only pure solvent. For the sake of clearness, the molecules are shown only as a single row. Normally there will be no passage of solvent molecules from side to side, for the average kinetic energy of the molecules on both sides is equal. This state of equilibrium is indicated on the diagram by marking with a cross the molecule which is exactly halfway through the partition.

At B a single solute molecule, S, has been introduced at the right side. If this molecule exactly cancels the energy of one solvent molecule at its own end of the row, the equi-

brium point will move one molecule to the right, the solvent molecules will move in the same direction, and one of their number will enter on the solution side. So long as the row includes one, and only one, solute molecule, the equilibrium will remain unchanged and no more solute molecules will pass in. If another solute molecule arrives on the scene, the equilibrium will again be disturbed in the same way as before, and another solvent molecule will pass into the solution.

This mechanism accomplishes to some extent the work of a "Maxwell Demon," in so far at least as it takes advantage of the movement of individual molecules to raise one part of a system at a uniform temperature to a higher level of energy.

A Mechanical View of Dissociation in Dilute Solutions.

The view that the phenomena of solution depend on the relative kinetic energy of the solvent and solute molecules appears to apply with special force to the phenomena of dissociation in dilute solutions. Under the gas theory there does not appear to be any reason why the solute molecules should dissociate into their ions. So obvious is this absence of any physical motive that Professor Armstrong has happily referred to the dissociation as "the suicides of the molecules." Others have proposed to ascribe the phenomenon to what might be called "the fickleness of the ions," thus supposing that the ions have an inherent love of changing partners. These may be picturesque ways of labelling certain views of the situation, but the views themselves do not appear to supply any clue to the physical nature of the phenomena. With the acceptance of the view that the phenomena of solution are largely due to the kinetic energy of the solvent molecules, the phenomena of dissociation also appear to take their place as a natural result of this activity. For consider the situation of an isolated molecule of cyanide of gold and potassium closely surrounded by and at the mercy of some millions of water molecules all in a state of intense activity. The rude mechanical jostling to which the complex molecule is subjected will naturally tend to break it up into simpler portions which are mechanically more stable. The mechanical analogy of a ball mill in which the balls are self-driven at an enormous velocity is probably rather crude, but it may at least help us to picture what, on the view now advanced, must be essentially a mechanical operation.

In importing this mechanical view of the breaking down of complex into simpler molecules we are not without some solid basis of facts to go upon. My own observations have shown that even in the solid state the crystalline molecule can be broken down by purely mechanical means into the simpler units of the amorphous state; and, further, that the water molecules of a crystal may by the same agency be broken away from their combination with the salt molecules. Since the publication of the earlier of these observations Professor Spring has shown that the acid sulphates of the alkali metals may be mechanically decomposed into two portions, one of which contains more acid, and the other more base than the original salt. It is important to recognise that in these three apparently short steps the transition has been made from the overcoming of the simple cohesion of similar molecules in contact with each other to the breaking asunder of the chemical union of dissimilar molecules. At each step the solid molecules appear, not as mere ethereal abstractions, but as substantial portions of matter which can be touched and handled mechanically.

The physical properties of a gas are primarily due to its being an assemblage of rapidly moving molecules. These simpler and more general properties can coexist with, and may be modified by, the more complex relations introduced by chemical affinity as it occurs in compound gases and mixtures.

It appears to me quite legitimate similarly to regard the physical properties of a liquid as due to its being an assemblage of rapidly moving molecules. The liquid system is

highly condensed, and the motions of its molecules are controlled by the cohesive as well as by the repulsive forces. The closer approximation of the molecules may reduce their mean free path to an extremely small amount, or it may even cause their translatory motion to disappear, so that the whole kinetic energy of the liquid molecules may be in the form of rotation or vibration.

As we can imagine a perfect gas, so also may we imagine a perfect liquid, the physical properties of which are as simply related to the laws of dynamics as are those of the gas. But the conditions of the liquid state being also those most favourable to the play of chemical affinity, the internal equilibrium of solutions or of mixed liquids must be a resultant of this affinity together with the primary forces of the ideal liquid state.

An ideally perfect solution—that is, a solution the physical properties of which are determined solely by the number of molecules it contains in a given volume—must consist of a solvent and a solute which have no chemical affinity for each other, so that their molecules will neither associate nor dissociate in solution. Probably only comparatively few solutions will be found which even approximate to this ideal perfection. But it appears to me that the study of the problems of the liquid and the dissolved states may be much simplified by the recognition (1) that the primary physical properties of liquids and solutions are due to the fact that they are assemblages of molecules endowed with the amount and the kind of kinetic energy which is proper to their temperature; and (2) that as these primary physical properties of the liquid and dissolved states may be masked and interfered with by chemical affinity, they should be studied as far as possible in examples where the influence of this force is either absent or at a minimum.

THE "THORIUM ACTIVITY" OF MONAZITE.

By F. GIESEL.

FROM the work of Elster and Geitel on the radio-active constituents of Baden-Baden mud (*Physikal. Zeit.*, 1905, vi., 67) and of Hahn and Sackur on the thorianite from Ceylon (*Berichte*, 1905, xxxviii., 1756) it follows that thorium itself does not seem to produce the emanation named after it.

Accordingly, it is also to be assumed that commercial thorium owes its activity to the presence of traces of an impurity of a far more active substance.

Experiments which I arranged some time ago with an artificial barium sulphate precipitate obtained from monazite cerium liquors (thorium had previously been completely removed) seem to confirm this. This precipitate, which carries down the rare earths with it, had been obtained incidentally two years ago during the working up of 30 k.grms. of monazite sand, and was given to me through the kindness of Herr Przibylla. The activity of the product was about double that of thorium oxalate,* and the decay constant of the induction was identical with that of thorium.

From 1 k.grm., the greater part of the barium sulphate precipitate, the earths, after being converted into chloride, were separated from the barium by means of ammonia; as oxalates they weighed 115 grms. On being converted into chloride a small quantity of sulphate remained behind undecomposed. It appeared that the activity was considerably concentrated in this residue, while that of the 115 grms. had greatly diminished. The ammonia precipitate of the rare earths obtained as above from this

* In the determination of the activity of the preparation in Elster and Geitel's apparatus, just as with emanium preparations, we have to take into account the variations in the power of emanation, which are dependent upon the chemical condition. For example, thorium oxide obtained by igniting the oxalate gave a leakage about five times as great as that of the oxalate. Thorium hydroxide obtained by precipitation with caustic potash at once gave a leakage fifty times as great as that of the oxalate used.

sulphate was decomposed while still moist by means of ammonium carbonate into a soluble portion of 0.1 grm. (as oxalate) and an insoluble portion of 2 grms. (as oxalate).

The latter 2 grms. contained chiefly cerium. After ignition of the oxalates there remained 0.12 grm. undissolved in nitric acid; 0.65 grm. were precipitated with permanganate and magnesia, and the filtrate gave 0.03 grm. of oxalate as the part richest in lanthanum.

The former 0.1 grm. of oxalate must contain the thorium; it was extracted with ammonium oxalate, and gave 6 m.grms. of oxalate residue and 0.04 grm. of hydroxide from the filtrate. The hydroxide might be considered to be thorium.

The examination in the leakage apparatus of the preparations thus separated showed that the further chemical separations had not appreciably affected the activity; they all gave a value about ten times as high as that of thorium hydroxide. The preparations do not excite the luminescent screen, as a barium-radium preparation of equal leakage does, probably because the discharging effect is due essentially to the emanation.

Elster and Geitel have kindly determined the decay constants of the induction of most of the preparations. With the 0.65 grm. of the cerium precipitate the induced activity showed the increase characteristic of thorium, shortly after the end of the exposure. The decay of the emanation itself was also determined, and it was found that it disappears almost entirely in an hour. The physical properties resemble those of the preparation obtained by Elster and Geitel from the Baden-Baden mud.

From these experiments it follows that the "thorium activity" of monazite is not to be ascribed to thorium itself, and that it may even reach a higher value in preparations which are practically free from thorium.

Addendum.—As a supplement to my article in these *Berichte* (1905, xxxviii., 707) it may be mentioned that from cerium earths containing emanium, by repeated crystallisation of the magnesium double nitrates, the lanthanum salt can be obtained free from emanium (thus inactive).

Emanium X can be completely precipitated by means of artificial barium sulphate from neutral chloride solution of the rare earths (free from thorium), so that after precipitation of these earths by ammonia, the presence of EX can no longer be detected either in the hydroxides nor in the filtrate.—*Berichte*, 1905, xxxviii., 2334.

ACTINIUM AND EMANIUM.

By W. MARCKWALD.

It is well known that Debierne (*Comptes Rendus*, 1899, cxxix., 593) discovered in pitchblende a radio-active substance, which follows the reactions of thorium and is characterised by the high power of emanation, and which he called actinium. Afterwards, Giesel (*Berichte*, 1902, xxxv., 3608) found in the rare earths separated from radium mother-liquors a substance which accompanies lanthanum, and which he named emanium on account of its extraordinary power of emanation.

More recently the identity of actinium and emanium was first affirmed by Debierne (*Comptes Rendus*, 1904, cxxxix., 14), and afterwards admitted with certain reservations by Giesel (*Berichte*, 1904, xxxvii., 3963). Finally, Sackur and Hahn (*Berichte*, 1905, xxxviii., 1943) showed that the decay constants of actinium and emanium agreed, and hence they concluded for this reason also that the two substances are identical.

An investigation of the rare earths, which we separated from radium mother-liquors, and 40 grms. of which were placed at my disposal by the firm of Dr. Rich. Sthamer, of Hamburg, most unexpectedly provided an elucidation of this question. These earths, which gave off considerable emanation, were converted into chlorides, and the thorium was separated in the usual way by means of thiosulphate.

There was only a very small quantity of this thorium, amounting to 0.7 grm. It gave off the emanation very strongly, and the emanation showed the characteristic short duration of life, which was not measured accurately. Thus I had obtained a specimen of actinium.

From the solution which had been freed from thorium, the cerium was first separated (by Mosander's method), and then the didymium and lanthanum were together separated as oxalates, and again converted into oxides. Neither the cerium oxide nor the mixture of didymium and lanthanum oxides showed any appreciable power of emanation.

The thorium from the thiosulphate precipitate was again purified by dissolving in hydrochloric acid, precipitated in oxalic acid, and the oxalate was then dissolved in ammonium oxalate. After filtering off the very small residue, the thorium oxalate was precipitated from the solution by acidifying, and converted into oxide by ignition. In all these operations the emanating substance had followed thorium.

By taking observations for several months it was found that this actinium lost its power of emanation as well as its radio-activity. While the cerium oxide preserved its small residual activity during the period mentioned, in the case of the mixture of didymium and lanthanum oxides the power of emanation appeared again at the same rate as it decayed in the case of the thorium oxide, till finally the latter only showed the emanation very slightly, and the didymium-lanthanum oxide, on the contrary, showed it very strongly.

Thus we have a case similar to that which has been completely investigated and explained by the beautiful researches of Rutherford and Soddy on the relation of thorium to thorium X. A radio-active substance follows lanthanum—for didymium according to Giesel's researches is indifferent—and its decay product is a second substance allied to thorium in its chemical reactions. This second substance is further decomposed, giving a strong emanation.

It is easy to show that this view corresponds to the facts. As after a period of some months the mixture of lanthanum and didymium oxides freed from thorium—amounting to 18 grms.—again gave the emanation strongly, it was dissolved in hydrochloric acid together with 0.5 grm. of ordinary thorium oxide, and the thorium was again precipitated with thiosulphate. The precipitate then contained almost all the carrier of the power of emanation, and the didymium-lanthanum oxide mixture again obtained from the solution was only feebly active.

In his most recent article on this subject Giesel (*Berichte*, 1905, xxxviii., 775) has alluded to the existence of an emanium X, which remains in the solution when lanthanum-emanium oxide is precipitated by ammonia. Hence the behaviour of the strongly emanating thorium obtained as above was investigated when it was precipitated with ammonia. It then appeared that the thorium hydroxide thus separated still gave the same strong emanation, while the solution, after it had been evaporated and the ammonium salts had been driven off, left no appreciable emanating residue.

From the foregoing it follows that actinium and emanium are not identical, but stand in a genetic relation. Emanium, if we designate thus the substance following lanthanum, produces actinium, the strongly emanating substance following thorium. The name emanium is not at all well chosen, for this substance gives no emanation whatever. It would have been better to name actinium from its power of emanation.

Such unsuitable names would be avoided if all the chemists engaged in research in the province of radio-activity would refrain from naming newly discovered substances until their properties had been thoroughly investigated. If insufficiently characterised substances are provided with names, complication results instead of simplification. Besides the example in question we may call attention to the case of polonium.—*Berichte*, 1905, xxxviii., 2264.

THE OXIDATION OF SULPHITES BY IODINE IN ALKALINE SOLUTION.

By R. HARMAN ASHLEY.

ACCORDING to Bunsen, Dupasquier's method of oxidising sulphurous acid by iodine in an acid solution, proceeds to completion according to the equation $2\text{SO}_2 + 2\text{I}_2 + 4\text{H}_2\text{O} = 4\text{HI} + 2\text{H}_2\text{SO}_4$ only when the concentration of the sulphur dioxide does not exceed 0.5 per cent of the solution. When, on the other hand, the proportion of sulphur dioxide exceeds this value, there is a secondary reaction, which, according to Volhard, involves the reduction of the sulphur dioxide by the hydriodic acid produced. This difficulty may be obviated, however, as has been shown by Volhard (*Ann. Chem.*, ccxlii, 93), if the solution of the sulphurous acid or a sulphite is run (with stirring) into a solution of iodine in potassium iodide, acidified with hydrochloric acid, to the bleaching of colour, using starch as an indicator—a procedure which is obviously less convenient than direct titration by a standard solution of iodine.

It has been recently further proposed by E. Rupp (*Ber.*, xxxv., 3694) to accomplish the oxidation in an alkaline solution, by treating the solution of sulphur dioxide or a sulphite with an excess of standard iodine in presence of acid sodium carbonate (1 grm.) during an interval of fifteen minutes, and determining the excess of iodine with sodium thiosulphate. Rupp's analytical examples, three in number, involving amounts of sulphur dioxide approximating 0.0343 grm., show small errors of excess, and from them the conclusion is drawn that sulphites, like arsenites, may be estimated in a solution made alkaline with sodium bicarbonate by the process indicated.

This very unusual use of sodium thiosulphate for the determination of free iodine in the presence of an alkali bicarbonate, suggests the question as to whether the sulphite was in reality completely oxidised by the treatment, or whether the apparently good results were in fact due to a chance balancing of errors of incomplete oxidation of the sulphite on the one hand, and, on the other hand, of the excessive use of iodine in the action of the thiosulphate in an alkaline solution, it being generally supposed that, in alkaline solutions, not only is the expected tetrathionate formed, but that some of the thiosulphate is oxidised to the extent of forming sulphate rather than tetrathionate exclusively.

In Table I. are data of experiments upon the action of iodine and sodium thiosulphate in alkaline solution. The sodium thiosulphate, approximately N/10, was standardised against approximately N/10 iodine solution in a neutral solution. Varying amounts of a saturated solution of acid sodium carbonate were used to render the solution alkaline in the experiments recorded.

TABLE I.

Iodine solution		=	0.01236	grm. per c.c.	
Sodium thiosulphate solution		=	0.01516	"	"
No.	$\text{Na}_2\text{S}_2\text{O}_3$, nearly N/10.	Iodine, nearly N/10.		Error in terms of I.	NaHCO_3 .
	I value.				
	C.c.	Grm.	C.c.	Grm.	
1.	11.94	0.1451	15.00	0.1854	+0.0403 20 c.c.
2.	11.69	0.1421	15.00	0.1854	+0.0433 20 "
3.	11.18	0.1359	15.00	0.1854	+0.0495 40 "
4.	11.25	0.1367	15.00	0.1854	+0.0487 40 "
5.	9.18	0.1116	11.00	0.1360	+0.0244 1 grm.
6.	9.11	0.1107	11.00	0.1360	+0.0253 1 "
7.	15.00	0.1823	15.98	0.1975	+0.0152 20 c.c.
8.	15.00	0.1823	16.31	0.2016	+0.0193 20 "
9.	15.00	0.1823	16.62	0.2054	+0.0231 40 "
10.	15.00	0.1823	16.65	0.2058	+0.0235 40 "

Treatment.—Nos. 1—6: Na₂S₂O₃ into iodine. Nos. 7—10: Iodine into Na₂S₂O₃.

It is plainly evident from Table I. that more iodine is used up in the presence of an alkali bicarbonate, whether the iodine is run into the thiosulphate or the thiosulphate into the iodine, than accords with the theory of the reaction.

Experiments were now undertaken for the purpose of contrasting the results obtained by Rupp's procedure with results found by oxidising the sulphite with iodine in an alkaline solution and determining the excess of iodine by standard arsenite, which, as is well known, acts with regularity upon iodine in the presence of an acid sodium carbonate. The volumes of the solutions at the time of oxidation varied from 25 to 50 c.c. The results are given in Table II.

TABLE II.

Rupp's Procedure.

Iodine value of SO ₂ taken.	Iodine taken.	Iodine value of Na ₂ S ₂ O ₃ taken.	NaHCO ₃ taken.	Error in terms of iodine.	Error in terms of SO ₂ .
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
0.0977	0.2474	0.1492	I	+0.0005	+0.0001
0.0977	0.2474	0.1454	I	+0.0043	+0.0011
0.1440	0.2969	0.1528	I	+0.0001	0.0000
0.1440	0.2969	0.1518	I	+0.0011	+0.0003
0.2759	0.4316	0.1582	I	-0.0025	-0.0006
0.2759	0.4316	0.1628	I	-0.0071	-0.0018

Excess of Iodine Determined by Standard Arsenite.

		Iodine value of arsenite taken.			
Iodine value of SO ₂ taken.	Iodine taken.	Iodine value of Na ₂ S ₂ O ₃ taken.	NaHCO ₃ taken.	Error in terms of iodine.	Error in terms of SO ₂ .
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
0.0977	0.2495	0.1543	I	-0.0025	-0.0006
0.0977	0.2495	0.1540	I	-0.0022	-0.0006
0.1440	0.2984	0.1586	I	-0.0042	-0.0010
0.1440	0.3017	0.1607	I	-0.0030	-0.0008
0.2759	0.4354	0.1710	I	-0.0115	-0.0029
0.2759	0.4354	0.1742	I	-0.0147	-0.0037

From a comparison of the results in the second section of Table II. with those in the first section, it appears that, under the conditions advocated by Rupp, the sulphite is not completely oxidised by the iodine. It seems that enough of the secondary action, by which the thiosulphate is oxidised beyond the condition of tetrathionate, takes place to counterbalance the error of incomplete oxidation when moderate amounts of sulphurous acid are handled, and more than enough for the smallest amounts, the secondary error predominating in such cases.

The results of experiments in which acid potassium carbonate was substituted for the acid sodium carbonate gave similar results.

So it appears that when Rupp's process gives results approximating the truth, it is due to the happy balancing of opposed errors. It seems quite possible that the same balancing of errors likewise occurs in the process for the determination of phosphorous acid described by Rupp and Fink (*Ber.*, 1902, xxxv., 3691).

In conclusion, I would like to thank Prof. F. A. Gooch for many kind suggestions.—*American Journal of Science*, 1905, xix., p. 237.

NOTICES OF BOOKS

Outlines of Inorganic Chemistry. By FRANK AUSTIN GOOCH and CLAUDE FREDERIC WALKER. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1905.

As a text-book for use in schools and colleges this book appears to be well above the average, especially when its very moderate price is taken into account. It is divided into two parts; in the first, and inductive part, dealing with the principles of chemistry, the development of modern theories is traced very logically, and if supplemented by a good course of practical work it should enable the student to acquire a thorough knowledge of chemical theory. One

of the chief merits of the book is the excellent balance preserved between detail and generalisation, so that neither is in the least degree sacrificed to the other. The second part of the book, which we should imagine would be read by the student side by side with the first, contains a systematic account of the elements and their chief compounds. The summaries of the most important properties and reactions of the various substances will be found of great use by examination candidates in co-ordinating their knowledge, as will also the paragraphs describing the characteristics of the natural groups. The book as a whole, although in some respects recalling the old familiar type of purely descriptive text book, crammed full of information, manages to maintain a decidedly higher level than these, and will be found worth keeping for reference even in a library containing far larger and more pretentious works.

Nieuwe Verhandelingen van het Bataafsch Genootschap der Proefondervindelijke Wijsbegeerte te Rotterdam. ("Recent Transactions of the Batavian Society of Experimental Science at Rotterdam"). Second Series. Vol. VI. Part I. Rotterdam: W. J. Van Hengel. 1905.

THIS volume of the "Transactions of the Batavian Scientific Society" contains two of the essays to which the gold medals of the Society have been awarded. The first of these papers, by Dr. C. W. Broers, contains a description of the author's experiments dealing with the duration of the virulence of tuberculous bacilli in milk, butter-milk, and butter respectively. Before attacking his subject the author appears to have carefully consulted all the necessary authorities, and to have arranged and performed his experiments with the utmost care. The second essay is entitled "An Inquiry into the Nature of the Sugar of some Vegetable Glucosides," and in it are described investigations of the action of emulsine upon various glucosides, such as arbutin, coniferin, æsculin, &c. Though the author does not appear to have arrived at any results which may be regarded as of great importance, the inquiry has obviously been well planned and carefully carried out.

Hypochlorite und Elektrische Bleiche. ("Hypochlorites and Electric Bleaches"). By Dr. EMIL ABEL. Halle-a-S.: Wilhelm Knapp. 1905.

THIS is a companion volume to an earlier one of the same series, by Viktor Engelhardt, which deals with the technical aspect of the subject, while Dr. Abel's work is occupied entirely with the theory of the preparation of bleaching liquors by electrochemical means, which really amounts to nothing more than the electrochemistry of solutions of the salts of hypochlorous acid. In considering this theory an unusually large number of factors has to be taken into account, and the thorough understanding of it necessitates the following of a fairly complicated explanation, which, however, Dr. Abel puts forward in as clear a manner as possible. He is always particularly careful to emphasise the difference between conclusions which have been proved experimentally on the one hand, and hypotheses and assumptions on the other, and he has incorporated in the volume the results of the most recent experiments, so that it forms a valuable and up-to-date guide to the preparation of bleaching liquors electrolytically.

Verflüssigtes Ammoniak als Lösungsmittel. ("Liquefied Ammonia as a Solvent"). By J. BRONN. Berlin: Julius Springer. 1905.

THE author of this monograph has endeavoured to give a complete account of all that is known of the use of liquid ammonia, and he hopes that he will thus awake additional interest in it as a solvent, and render reference to original publications dealing with its properties and applications superfluous. With this aim in view he has carefully collected all available information on the subject, and has

produced a most systematic review of the properties, both physical and chemical, of the liquid. He calls attention specially to its value from a technical point of view, and emphasises the fact that there is no serious difficulty in obtaining apparatus suitable for working with it, for it does not attack the heavy metals generally used for constructing apparatus, and at ordinary temperatures the pressure amounts to only 6 to 10 atmospheres.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 4, July 24, 1905.

Nature of the Hydrocyanic Glucoside obtained from Black Elder.—L. Quignard and J. Houdas.—The authors make an extract of the leaves of black elder. From the liquid obtained on the addition of semicarbazide a crystalline precipitate is formed. This semicarbazone is collected, dried, and re-crystallised from ether. Its analysis shows it to have the formula $\text{NH}_2\text{—CO—NH—N—CH—C}_6\text{H}_5$. When treated with HCl it decomposes, giving a liquid product boiling at 179° and having the characteristic smell of bitter almonds. These experiments therefore prove the leaves of black elder to contain amygdaline.

Catalytic Decomposition of Monochlor-formenic Derivatives in contact with Anhydrous Metallic Chlorides.—Paul Sabatier and A. Mailhe.—The authors find that the various anhydrous chlorides of the divalent metals (nickel, cobalt, iron, cadmium, lead, barium, &c.) act catalytically between the temperatures 260° and 300° on the primary monochlor-formenic derivatives, causing the latter to split up into hydrochloric acid and the corresponding ethylenic carbide. It is also evident that the secondary and tertiary derivatives, obtained by a single heating, undergo still more easily the same decomposition.

Fluorescence.—C. Camichel.—The experiments described in this paper prove that the intensity of the light emitted by fluorescence is proportional to the intensity of the exciting source of light. The author also verifies, by a new method, the already enunciated fact that the coefficient of absorption of a fluorescent body does not vary at the moment of fluorescence.

Influence of Water Vapour on the Reduction of Carbonic Anhydride by means of Carbon.—O. Boudouard.—The author performs a series of experiments to show the effect of the presence of water vapour on the reduction of carbon dioxide at temperatures between 650° and 1000° .

Synthesis of Zinc Silicates.—A. Duboin.—The zinc oxide is reacted upon by silica, the latter being dissolved in melted potassium fluoride. The products may be separated by means of the heavy solution of sodium iodide (a density of 3.46 being obtained). The first silicate has the formula $\text{K}_2\text{O}, 6\text{ZnO}, 4\text{SiO}_2$ and density 3.68. The second, formula $8\text{K}_2\text{O}, 9\text{ZnO}, 17\text{SiO}_2$ and density 2.96.

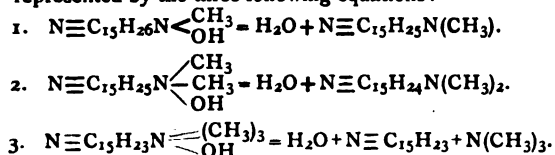
A Phosphorus Sub-iodide, and the Part Played by this Body in the Allotropic Transformation of Phosphorus.—R. Boulouch.—The author prepares a sub-iodide of phosphorus by the action of solar light on a mixture of iodine and phosphorus dissolved in very dry carbon disulphide. If the proportion of iodine is greater than would be present in the bi-iodide no effect is produced, but for less proportions of iodine a red precipitate is formed, which is produced more rapidly as the solution becomes more concentrated. This precipitate is collected and dried in a current of CO_2 at 100° , and its properties examined. To explain the catalytic action of this compound, at a high temperature (nearly 160°) the produc-

tion of bi-iodide of phosphorus is immediately followed by a reduction of this body by the white phosphorus. The iodide, PI_2 , becomes transformed into the sub-iodide in virtue of the necessarily exothermic reaction $7P(\text{white}) + PI_2 = 2P_4I$; but, at 160° and above, the P_4I decomposes, forming once again the bi-iodide, more or less dissociated, $2P_4I = PI_2 + 7P(\text{red})$. This is also an exothermic reaction.

Potassium Iridio-chloro-nitrite.—L. Quennessen.—The author treats the double nitrite of iridium and potassium with dilute hydrochloric acid. This treatment is repeated several times; then the liquid evaporated, dried, and re-dissolved in water saturated with potassium chloride. A precipitate is given which, when purified, is seen to consist of little yellow crystals which act on polarised light. Analysis proves them to be of the composition $Ir_3Cl_{16}(NO_2)_8K_{12} \cdot 4H_2O$.

Action of Sodium Sulphite on Ethanal.—MM. Seyewetz and Bardin.—Sodium sulphite and ethanal, which have no action on each other in dilute solution, react violently when they are mixed in concentrated solution. The author investigates the best conditions for production of crotonic aldehyde by varying systematically the temperature of the reaction, the proportion of the reagents, the time of contact, and the concentration of the solutions.

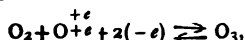
Sparteine: Hydrates of Methyl-, Dimethyl-, and Trimethyl-sparteinium.—Charles Moureu and Amand Valeur.—The authors investigate a series of reactions represented by the three following equations:—



Gentiine.—Georges Tanret.—Gentiine corresponds to the formula $C_{25}H_{28}O_{14}$. It is the first glucoside known which gives xylose amongst its products of decomposition. Its rarity has not yet enabled the author to thoroughly investigate the relations which exist between gentiine and gentiine.

Chemical Equilibrium of a System. Ammonia Gas and Primary Isoamylamine Chlorohydrate.—Félix Bidet.—Unsuitable for abstraction.

ERRATUM.—P. 63, col. 1. Instead of " $O + 2O$," &c., the formula should read as follows:—



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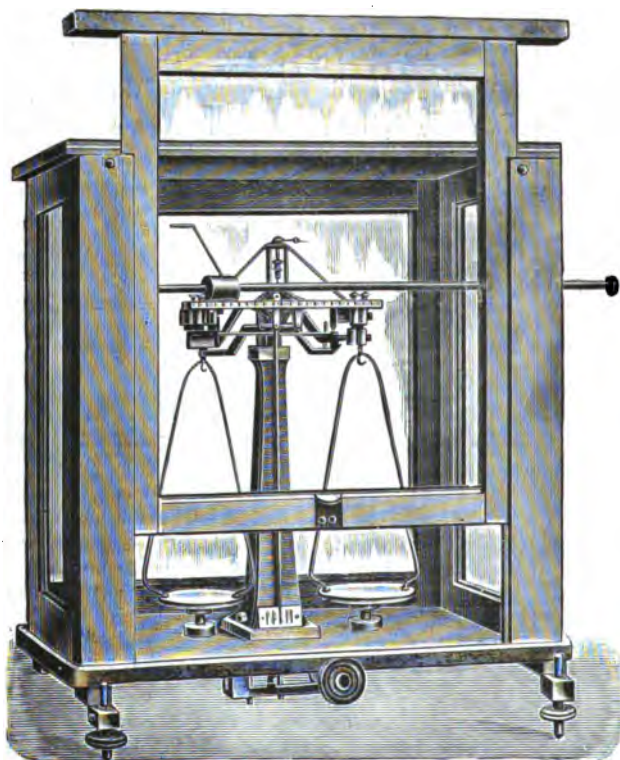
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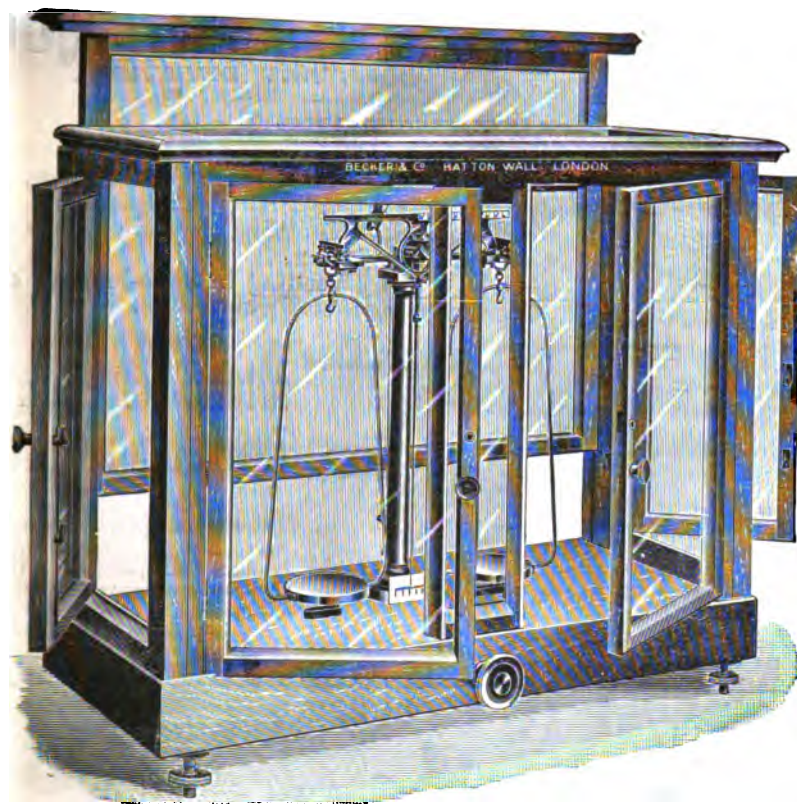
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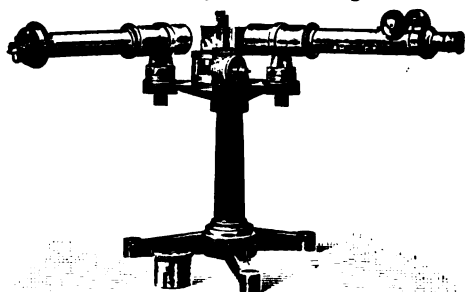
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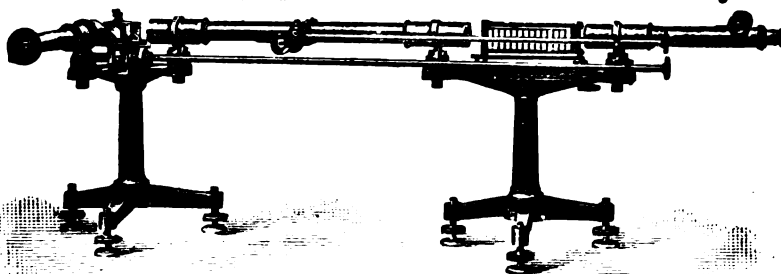
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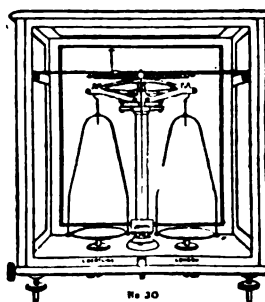
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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SOUTH AFRICA, 1905.

SECOND PART OF ADDRESS OF THE PRESIDENT,
Prof. G. H. DARWIN, M.A., LL.D., Ph.D., F.R.S.
(Delivered at JOHANNESBURG, August 30th).

At Cape Town I attempted to make a general survey of evolution in its various branches, and laid down certain general propositions as to what seems common to all of them.

I then went on to consider how these general laws found an application in the most recent speculations as to the constitution of matter. The atoms of the elements and the molecules of chemical combinations are constructed on so minute a scale that it is no easy task to picture them to our minds. On the other hand, we see in the heavens arrangements of matter on a scale so vast that it is equally difficult to grasp. Both the inconceivably small and the inconceivably large should fall under a general law, if it is a true one; and the history of satellites, planets, and stars present at least as great an interest as that of atoms and molecules. Accordingly, the transition from the small to the large seemed to afford a convenient halting place in my Address, and I propose to-night to resume the discussion by considering various theories of celestial evolution. But I will first try to render the point of view intelligible which I desire to take. A short preliminary explanation for those who were not at Cape Town thus becomes necessary.

I desire to present the essential features which are common to evolution in all its branches, and this may be done most easily by reference to political institutions, because we all fancy we understand something of politics.

The complex interactions of man with man in a community are usually described by such comprehensive terms as "the State," "the Commonwealth," or "the Government." Various States differ widely in their constitution and in the degree of the complexity of their organisation, and we classify them by various general terms, such as "autocracy," "aristocracy," or "democracy," which express somewhat loosely their leading characteristics. But for the purpose of showing the analogy with physics we need terms of wider import than those habitually used in politics. All forms of the State imply inter-relationship in the actions of men, and action implies movement. Thus the State may be described as a configuration or arrangement of a community of men; or we may say that it implies a definite mode of motion of men—that is to say, an organised scheme of action of man on man. Political history gives an account of the gradual changes in such configurations or modes of motion of men as have possessed the quality of persistence or of stability to resist the disintegrating influence of surrounding circumstances.

In the history of a State we find this stability or power of persistence continually changing. It slowly rises to a maximum, and then declines; when it falls to nothing a revolution ensues, and a new form of government is established. This new mode of motion of men, or government, has at first but little stability, but it gradually acquires strength and permanence, until in its turn the slow decay in the power of persistence leads on to a new revolution. Such crises in political history may give rise to a condition in which the State is incapable of perpetuation

by transformation. This occurs when a savage tribe nearly exterminates another and leads the few survivors into slavery; the previous form of government then becomes extinct.

Now turn to the evolution of the various forms of life. The fundamental idea in the theory of Natural Selection is the persistence of those types of life which are adapted to their surrounding conditions, and the elimination by extermination of the ill-adapted types. The struggle for life amongst forms possessing various degrees of adaptation to slowly varying conditions is held to explain the transmutation of species. Although a different phraseology is used when we speak of the physical world, yet the idea is essentially the same. Theories of physical evolution involve the discovery of modes of motion or configurations of matter which are capable of persistence. The physicist describes such types as stable; the biologist calls them species.

The physicist, the biologist, and the historian alike watch the effect of slowly varying external conditions; they all observe the rise and decline of stability, with the consequent change of type of motion, transmutation of species, or revolution.

And now after this preface I turn to astronomical theories of evolution.

The German astronomer Bode long ago propounded a simple empirical law concerning the distances at which the several planets move about the sun, and his formula embraces so large a number of cases with accuracy that we are compelled to believe that it arises in some manner from the primitive conditions of the planetary system.

The explanation of the causes which have led to this simple law as to the planetary distances presents an interesting problem, and, although it is still unsolved, we may obtain some insight into its meaning by considering what may be called a working model of ideal simplicity.

Imagine, then, a sun round which there moves in a circle a single large planet. I will call this planet Jove, because it may be taken as a representative of our largest planet, Jupiter. Suppose next that a meteoric stone or small planet is projected in any perfectly arbitrary manner in the same plane in which Jove is moving; then we ask how this third body will move. It appears that under the combined attractions of the sun and Jove the meteoric stone will in general describe an orbit of extraordinary complexity, at one time moving slowly at a great distance from both the sun and Jove, at other times rushing close past one or other of them. As it grazes past Jove or the sun it may often but just escape a catastrophe, but a time will come at length when it runs it chances too fine and comes into actual collision. The individual career of the stone is then ended by absorption, and of course by far the greater chance is that it will find its Nirvana by absorption in the sun.

Next let us suppose that instead of one wandering meteoric stone or minor planet there are hundreds of them, moving initially in all conceivable directions. Since they are all supposed to be very small, their mutual attractions will be insignificant, and they will each move almost as though they were influenced only by the sun and Jove. Most of these stones will be absorbed by the sun, and the minority will collide with Jove.

When we inquire how long the career of a stone may be, we find that it depends on the direction and speed with which it is started, and that by proper adjustment the delay of the final catastrophe may be made as long as we please. Thus by making the delay indefinitely long we reach the conception of a meteoric stone which moves so as never to come into collision with either body.

There are, therefore, certain perpetual orbits in which a meteoric stone or minor planet may move for ever without collision. But when such an immortal career has been discovered for our minor planet, it still remains to discover whether the slightest possible departure from the prescribed orbit will become greater and greater, and ultimately lead to a collision with the sun or Jove, or whether the body will

travel so as to cross and re-cross the exact perpetual orbit, always remaining close to it. If the slightest departure inevitably increases as time goes on, the orbit is unstable; if, on the other hand, it only leads to a slight waviness in the path described, it is stable.

We thus arrive at another distinction; there are perpetual orbits, but some, and indeed most, are unstable, and these do not offer an immortal career for a meteoric stone; and there are other perpetual orbits which are stable or persistent. The unstable ones are those which succumb in the struggle for life, and the stable ones are the species adapted to their environment.

If, then, we are given a system of a sun and large planet together with a swarm of small bodies moving in all sorts of ways, the sun and planet will grow by accretion, gradually sweeping up the dust and rubbish of the system, and there will survive a number of small planets and satellites moving in certain definite paths. The final outcome will be an orderly planetary system in which the various orbits are arranged according to some definite law.

There is hardly room for doubt that if a complete solution for our solar system were attainable, we should find that the orbits of the existing planets and satellites are numbered amongst the stable perpetual orbits, and should thus obtain a rigorous mechanical explanation of Bode's law concerning the planetary distances.

In the first portion of my Address I described the orbits in which the corpuscles move in the atoms of matter, and drew attention to the resemblance to a planetary system. It may not, perhaps, be fanciful to imagine that some general mathematical method devised for solving a problem of cosmical evolution may find another application to miniature atomic systems, and may thus lead onward to vast developments of industrial mechanics. Science, however diverse its aims, is a whole, and men of science do well to impress on the captains of industry that they should not look askance on those branches of investigation which may seem for the moment far beyond any possibility of practical utility.

The theory which I have now explained points to the origin of the sun and planets from gradual accretions of meteoric stones, and it makes no claim to carry the story back behind the time when there was already a central condensation or sun about which there circled another condensation or planet. But more than a century ago an attempt had already been made to re-construct the history back to a yet remoter past, and, as we shall see, this attempt was based upon quite a different supposition as to the constitution of the primitive solar system. I myself believe that the theory I have just explained, as well as that to which I am coming, contains essential elements of truth, and that the apparent discordances will some day be reconciled. The theory of which I speak is the celebrated Nebular Hypothesis, first suggested by the German philosopher Kant, and later re-stated independently and in better form by the French mathematician Laplace.

Laplace traced the origin of the solar system to a nebula or cloud of rarefied gas congregated round a central condensation which was ultimately to form the sun. The whole was slowly rotating about an axis through its centre, and, under the combined influences of rotation and of the mutual attraction of the gas, it assumed a globular form, slightly flattened at the poles. The primeval globular nebula is undoubtedly a stable or persistent figure, and thus Laplace's hypothesis conforms to the general laws which I have attempted to lay down.

The nebula must have gradually cooled by radiation into space, and as it did so the gas must necessarily have lost some of its spring or elasticity, thus permitting a greater degree of condensation of the whole. The contraction led inevitably to two results: first, the central condensation became hotter; and, secondly, the speed of its rotation became faster. The accelerated rotation led to an increase in the amount of polar flattening, and the nebula at length assumed the form of a lens, or of a disk thicker in the middle than at the edges. Assuming the existence

of the primitive nebula, the hypothesis may be accepted thus far as practically certain.

From this point, however, doubt and difficulty enter into the argument. It is supposed that the nebula became so much flattened that it could not subsist as a continuous aggregation of gas, and a ring of matter detached itself from the equatorial regions. The central portions of the nebula, when relieved of the excrescence, resumed the more rounded shape formerly possessed by the whole. As the cooling continued, the central portion in its turn became excessively flattened through the influence of its increased rotation; another equatorial ring then detached itself, and the whole process was repeated as before. In this way the whole nebula was fissured into a number of rings surrounding the central condensation, whose temperature must by then have reached incandescence.

Each ring then aggregated itself round some nucleus which happened to exist in its circumference, and so formed a subordinate nebula. Passing through a series of transformations, like its parent, this nebula was finally replaced by a planet with attendant satellites.

The whole process forms a majestic picture of the history of our system. But the mechanical conditions of a rotating nebula are too complex to admit, as yet, of complete mathematical treatment; and thus, in discussing this theory, the physicist is compelled in great measure to adopt the qualitative methods of the biologist, rather than the quantitative ones which he would prefer.

Although the telescope seems to confirm the general correctness of Laplace's hypothesis, yet it is hardly too much to say that every stage in the supposed process presents to us some impossibility.

Thus, for example, the ring of Saturn seems to have suggested the theory to Laplace; but to take it as a model leads us straight to a quite fundamental difficulty. If a ring of matter ever concentrates under the influence of its mutual attraction, it can only do so round the centre of gravity of the whole ring. Therefore the matter forming an approximately uniform ring, if it concentrates at all, can only fall in on the parent planet and be re-absorbed. Some external force other than the mutual attraction of the matter forming the ring, and therefore not provided by the theory, seems necessary to effect the supposed concentration. The only way of avoiding this difficulty is to suppose the ring to be ill-balanced or lop-sided; in this case, provided the want of balance is pronounced enough, concentration will take place round a point inside the ring but outside the planet.

However, this is not the time to pursue these considerations further, yet enough has been said to show that the Nebular Hypothesis cannot be considered as a connected intelligible whole, however much of truth it may contain.

In the first theory which I sketched as to the origin of the sun and planets, we supposed them to grow by the accretions of meteoric wanderers in space, and this hypothesis is apparently in fundamental disagreement with the conception of Laplace, who watches the transformations of a continuous gaseous nebula. I must not pause to consider how these seemingly discordant views may be reconciled, but will merely say that I conceive both theories contain important elements of truth.

We have seen that, in order to explain the genesis of planets according to Laplace's theory, the rings must be ill-balanced or even broken. If the ring were so far from being complete as only to cover a small segment of the whole circumference, the true features of the occurrences in the births of planets and satellites might be better represented by conceiving the detached portion of matter to have been more or less globular from the first, rather than ring-shaped. Now this idea introduces us to another group of researches whereby mathematicians have sought to explain the birth of planets and satellites.

The solution of the problem of evolution involves the search for those persistent or stable forms which biologists would call species. The species of which I am now going

to speak may be grouped in a family, which comprises all those various forms which a mass of rotating liquid is capable of assuming under the conjoint influences of gravitation and rotation. If the earth were formed throughout of a liquid of the same density, it would be one of the species of this family; and indeed these researches date back to the time of Newton, who was the first to explain the figures of planets.

The ideal liquid planets we are to consider must be regarded as working models of actuality, and inasmuch as the liquid is supposed to be incompressible, the conditions depart somewhat widely from those of reality. Hence, when the problem has been solved, much uncertainty remains as to the extent to which our conclusions will be applicable to actual celestial bodies.

We begin, then, with a rotating liquid planet like the earth, which is the first stable species of our family. We next impart in imagination more rotation to this planet, and find by mathematical calculation that its power of resistance to any sort of disturbance is less than it was. In other words, its stability declines with increased rotation, and at length we reach a stage at which the stability just vanishes. At this point the shape is a transitional one, for it is the beginning of a new species with different characteristics from the first, and with a very feeble degree of stability or power of persistence. As a still further amount of rotation is imparted, the stability of the new species increases to a maximum and then declines until a new transitional shape is reached and a new species comes into existence. In this way we pass from species to species with an ever-increasing amount of rotation.

The first or planetary species has a circular equator like the earth; the second species has an oval equator, so that it is something like an egg spinning on its side on a table; in the third species we find that one of the two ends of the egg begins to swell, and that the swelling gradually becomes a well-marked protrusion or filament. Finally, the filamentous protrusion becomes bulbous at the end, and is only joined to the main mass of liquid by a gradually thinning neck. The neck at length breaks, and we are left with two separate masses which may be called planet and satellite.

In this ideal problem the successive transmutations of species are brought about by gradual additions to the amount of rotation with which the mass of liquid is endowed. It might seem as if this continuous addition to the amount of rotation were purely arbitrary, and could have no counterpart in Nature. But real bodies cool and contract in cooling, and I must ask you to believe that the effects of an apparently arbitrary increase of rotation may be produced by cooling.

The figures which I succeeded in drawing, by means of rigorous calculation, of the later stages of this course of evolution, are so curious as to remind one of some such phenomenon as the protrusion of a filament of protoplasm from a mass of living matter, and I suggest that we may see in this almost life-like process the counterpart of at least one form of the birth of double stars, planets, and satellites.

My Cambridge colleague Jeans has also made an interesting contribution to the subject by attacking the far more difficult case where the rotating fluid is a compressible gas. In this case also he finds a family of types, but the conception of compressibility introduced a new set of considerations in the transitions from species to species. The problem is, however, of such difficulty that he had to rest content with results which were rather qualitative than strictly quantitative.

It cannot be doubted that the supposed Laplacian sequence of events possesses a considerable element of truth, yet these latter schemes of transformation can be followed in closer detail. It seems, then, probable that both processes furnish us with crude models of reality, and that in some cases the first and in others the second is the better representative.

The moon's mass is one-eightieth of that of the earth,

whereas the mass of Titan, the largest satellite in the solar system, is 1/4600 of that of Saturn. On the ground of this great difference between the relative magnitudes of all other satellites and of the moon, it is not unreasonable to suppose that the mode of separation of the moon from the earth may also have been widely different. The theory of which I shall have next to speak claims to trace the gradual departure of the moon from an original position not far removed from the present surface of the earth. If this view is correct, we may suppose that the detachment of the moon from the earth occurred as a single portion of matter, and not as a concentration of a Laplacian ring.

If a planet is covered with oceans of water and air, or if it is formed of plastic molten rock, tidal oscillations must be generated in its mobile parts by the attractions of its satellites and of the sun. Such movements must be subject to frictional resistance, and the planet's rotation will be slowly retarded by tidal friction in much the same way that a fly-wheel is gradually stopped by any external cause of friction. Since action and reaction are equal and opposite, the action of the satellites on the planet, which causes the tidal friction of which I speak, must correspond to a reaction of the planet on the motion of the satellites.

At any moment of time we may regard the system composed of the rotating planet with its attendant satellite as a stable species of motion, but the friction of the tides introduces forces which produce a continuous, although slow, transformation in the configuration. It is, then, clearly of interest to trace backwards in time the changes produced by such a continuously acting cause, and to determine the initial condition from which the system of planet and satellite must have been slowly degrading. We might also look forward, and discover whither the transformation tends.

Let us consider, then, the motion of the earth and moon revolving in company round the sun, on the supposition that the friction of the tides in the earth is the only effective cause of change. We are, in fact, to discuss a working model of the system, analogous to those of which I have so often spoken before; and it must suffice to set forth the result in its main outline as referring only to the past.

If we take the "day," regarding it as a period of variable length, to mean the time occupied by a single rotation of the earth on its axis, and the "month," likewise variable in absolute length, to mean the time occupied by the moon in a single revolution round the earth, the number of days in the month expresses the speed of the earth's rotation relatively to the speed of the moon's revolution.

Now in our retrospect both day and month are found continuously shortening; but as on the whole the month shortens much more quickly than the day, the number of days in the month also falls. We may, then, ask at once, What is the initial stage to which the gradual transformation points? I say, that on following the argument to its end the system may be traced back to a time when the day and month were identical in length, and were both only about four or five of our present hours. The identity of day and month means that the moon was always opposite to the same side of the earth; thus at the beginning the earth always presented the same face to the moon, just as the moon now always shows the same face to us. Moreover, when the month was only some four or five of our present hours in length, the moon must have been only a few thousand miles from the earth's surface—a great contrast with the present distance of 240,000 miles.

It might well be argued from this conclusion alone that the moon separated from the earth more or less as a single portion of matter at a time immediately antecedent to the initial stage to which she has been traced. But there exists a yet more weighty argument favourable to this view, for it appears that the initial stage is one in which the stability of the species of motion is tottering, so that the system presents the characteristic of a transitional form, which we have seen to denote a change of type or species in a previous case.

In discussing the transformations of a liquid planet we saw the tendency of the single mass to divide into two portions, and now we seem to reach a similar crisis from the opposite end, when in retrospect we trace back the system to two masses of unequal sizes in close proximity with one another. The argument almost carries conviction with it, but I have necessarily been compelled to pass over various doubtful points.

Time is wanting to consider other subjects worthy of notice which arise out of this problem, yet I wish to point out the fact that tidal friction is competent to explain the eccentricity of an orbit, because this conclusion has been applied in a manner to which I shall have occasion to return hereafter.

If, as has been argued, tidal friction has played so important a part in the history of the earth and moon, it might be expected that the like should be true of the other planets and satellites, and of the planets themselves in their relationship to the sun. But numerical examination of the several cases proves conclusively that this cannot have been the case. The relationship of the moon to the earth is in fact quite exceptional in the solar system, and we have still to rely on such theories as that of Laplace for the explanation of the main outlines of the solar system.

I have not yet mentioned the time occupied by the sequence of events sketched out in the various schemes of cosmogony, and the question of cosmical time is a thorny and controversial one.

Our ideas are absolutely blank as to the time requisite for the evolution either according to Laplace's nebular hypothesis, or the meteoritic theory. All we can assert is that they demand enormous intervals of time as estimated in years.

The theory of tidal friction stands alone amongst these evolutionary speculations in that we can establish an exact but merely relative time-scale for every stage of the process. Although it is true that the value in years of the unit of time remains unknown, yet it is possible to determine a period in years which must be shorter than that in which the whole history is comprised. If at every moment since the birth of the moon tidal friction had always been at work in such a way as to produce the greatest possible effect, then we should find that sixty million years would be consumed in this portion of evolutionary history. The true period must be much greater, and it does not seem unreasonable to suppose that 500 to 1000 million years may have elapsed since the birth of the moon. Such an estimate would not seem extravagant to geologists who have, in various ways, made exceedingly rough determinations of geological periods.

As far as my knowledge goes I should say that pure geology points to some period intermediate between 50 and 1000 millions of years, the upper limit being more doubtful than the lower. Thus far we do not find anything which renders the tidal theory of evolution untenable.

But the physicists have formed estimates in other ways which, until recently, seemed to demand in the most imperative manner a far lower scale of time. According to all theories of cosmogony, the sun is a star which became heated in the process of its condensation from a condition of wide dispersion. When a meteoric stone falls into the sun the arrest of its previous motion gives rise to heat, just as the blow of a horse's shoe on a stone makes a spark. The fall of countless meteoric stones, or the condensation of a rarefied gas, was supposed to be the sole cause of the sun's high temperature.

Since the mass of the sun is known, the total amount of the heat generated in it, in whatever mode it was formed, can be estimated with a considerable amount of precision. The heat received at the earth from the sun can also be measured with some accuracy, and hence it is a mere matter of calculation to determine how much heat the sun sends out in a year. The total heat which can have been generated in the sun divided by the annual output gives a quotient of about 20 millions. Hence it seemed to be im-

peratively necessary that the whole history of the solar system should be comprised within some 20 millions of years.

This argument, which is due to Helmholtz, appeared to be absolutely crushing, and for the last forty years the physicists have been accustomed to tell the geologists that they must moderate their claims. But for myself I have always believed that the geologists were more nearly correct than the physicists, notwithstanding the fact that appearances were so strongly against them.

And now, at length, relief has come to the strained relations between the two parties, for the recent marvellous discoveries in physics show that concentration of matter is not the only source from which the sun may draw its heat.

Radium is a substance which is perhaps millions of times more powerful than dynamite. Thus it is estimated that an ounce of radium would contain enough power to raise 10,000 tons a mile above the earth's surface. Another way of stating the same estimate is this:—The energy needed to tow a ship of 12,000 tons a distance of 6000 sea miles at 15 knots is contained in 22 ounces of radium. The Saxon probably burns five or six thousand tons of coal on a voyage of approximately the same length. Other lines of argument tend in the same direction.

Now we know that the earth contains radio-active materials, and it is safe to assume that it forms in some degree a sample of the materials of the solar system; hence it is almost certain that the sun is radio-active also.

This branch of science is as yet but in its infancy, but we already see how unsafe it is to dogmatise on the potentialities of matter. It appears, then, that the physical argument is not susceptible of a greater degree of certainty than that of the geologists, and the scale of geological time remains in great measure unknown.

I have now ended my discussion of the solar system, and must pass on to the wider fields of the stellar universe.

Only a few thousand stars are visible with the unaided eye, but photography has revealed an inconceivably vast multitude of stars and nebulae, and every improvement in that art seems to disclose yet more and more. It seems useless to consider whether the number of stars has any limit, for infinite number, space, and time transcend our powers of comprehension. We must then make a virtue of necessity, and confine our attention to such more limited views as seem within our powers.

A celestial photograph looks at first like a dark sheet of paper splashed with whitewash, but further examination shows that there is method in the arrangement of the white spots. Thus there is order of some sort in the heavens, and, although no reason can be assigned for the observed arrangement in any particular case, yet it is possible to obtain general ideas as to the succession of events in stellar evolution.

Besides the stars there are numerous streaks, wisps, and agglomerations of nebulosity, whose light we know to emanate from gas. Spots of intenser light are observed in less brilliant regions; clusters of stars are sometimes imbedded in nebulosity, while in other cases each individual star of a cluster stands out clear by itself. These and other observations force on us the conviction that the wispy clouds represent the earliest stage of development, the more condensed nebulae a later stage, and the stars themselves the last stage. This view is in agreement with the nebular hypothesis of Laplace, and we may fairly conjecture that chains and lines of stars represent pre-existing streaks of nebulosity.

Change is obviously in progress everywhere, as well in each individual nebula and star as in the positions of these bodies relatively to one another. But we are unable even to form conjectures as to the tendency of the evolution which is going on. This being so, we cannot expect, by considering the distribution of stars and nebulae, to find

many illustrations of the general laws of evolution which I have attempted to explain; accordingly, I must confine myself to the few cases where we at least fancy ourselves able to form ideas as to the stages by which the present conditions have been reached.

Up to a few years ago there was no evidence that the law of gravitation extended to the stars, and even now there is nothing to prove the transmission of gravity from star to star. But in the neighbourhood of many stars the existence of gravity is now as clearly demonstrated as within the solar system itself. The telescope has disclosed the double character of a large number of stars, and the relative motion of the pairs of companions has been observed with the same assiduity as that of the planets. When the relative orbit of a pair of binary or double stars is examined, it is found that the motion conforms exactly to those laws of Kepler which prove that the planets circle round the sun under the action of solar gravitation. A leading characteristic of all these double stars is that the two companions do not differ enormously in mass from one another. In this respect these systems present a strongly marked contrast with that of the sun, attended as it is by relatively insignificant planets.

In the earlier part of my Address I showed how theory indicates that a rotating fluid body will as it cools separate into two detached masses. Mathematicians have not yet been able to carry their analysis far enough to determine the relative magnitudes of the two parts, but as far as we can see the results point to the birth of a satellite whose mass is a considerable fraction of that of its parent. Accordingly, See (who devotes his attention largely to the astronomy of double stars), Alexander Roberts, and others consider that what they have observed in the heavens is in agreement with the indications of theory. It thus appears that there is reason to hold that double stars have been generated by the division of primitive and more diffused single stars.

But if this theory is correct we should expect the orbit of a double star to be approximately circular; yet this is so far from being the case that the eccentricity of the orbits of many double stars exceeds by far any of the eccentricities in the solar system. Now, See has pointed out that when two bodies of not very unequal masses revolve round one another in close proximity, the conditions are such as to make tidal friction as efficient as possible in transforming the orbit. Hence we seem to see in tidal friction a cause which may have sufficed not only to separate the two component stars from one another, but also to render the orbit eccentric.

I have thought it best to deal very briefly with stellar astronomy in spite of the importance of the subject, because the direction of the changes in progress is in general too vague to admit of the formation of profitable theories.

We have seen that it is possible to trace the solar system back to a primitive nebula with some degree of confidence, and that there is reason to believe that the stars in general have originated in the same manner. But such primitive nebulae stand in as much need of explanation as their stellar offspring. Thus, even if we grant the exact truth of these theories, the advance towards an explanation of the universe remains miserably slight. Man is but a microscopic being relatively to astronomical space, and he lives on a puny planet circling round a star of inferior rank. Does it not, then, seem as futile to imagine that he can discover the origin and tendency of the universe as to expect a housefly to instruct us as to the theory of the motions of the planets? And yet, so long as he shall last, he will pursue his search, and will no doubt discover many wonderful things which are still hidden. We may, indeed, be amazed at all that man has been able to find out, but the immeasurable magnitude of the undiscovered will throughout all time remain to humble his pride. Our children's children will still be gazing and marvelling at the starry heavens, but the riddle will never be read.

ON THE

REFRACTIVE INDEX OF GASEOUS FLUORINE.*

By C. CUTHBERTSON and E. B. R. PRIDEAUX, M.A., B.Sc.

THE authors have determined the refractive index of gaseous fluorine for sodium light by means of Jamin's refractometer. Five experiments gave values for the refractivity $(\mu - 1)10^6$ of 195, 177, 192, 194, and 198½. The discrepancy exhibited by the second experiment can be accounted for, and it is believed that the mean of the other four experiments, 195, is within 2 or 3 per cent of the true value.

The gas was prepared in a copper electrolytic tube, similar to that used by M. Moissan, and, after being purified from the vapour of hydrofluoric acid and from ozone, was made to displace dry air from a refractometer tube of platinum-iridium, whose ends were closed by plates of fluorspar. It was found by experience that it was impossible to obtain the gas completely free from air, or oxygen produced during electrolysis, and it was necessary, therefore, to analyse the mixture of gases contained in the refractometer tube at the moment when the index was observed.

The method employed for this purpose was to bring the gases into contact with dry lead filings in a closed space, and to estimate the volume of fluorine from the contraction. When the refractometer tube was filled with the gases produced by electrolysis it was disconnected from the source of supply, and its exit and entry tubes rapidly connected with two closed burettes, half filled with mercury, having at their upper extremities a narrow tube containing a large quantity of dry lead filings. Each closed burette was in communication with an open tube, and one was also connected with a reservoir of mercury. The open tubes were connected by a wire passing over a pulley, so that, when one was raised the other fell by an equal height. By moving these tubes the mixture of gases in the refractometer tube was pushed into the tube containing the lead filings, where the fluorine was absorbed as lead fluoride. As contraction occurred the pressure was equalised by letting in mercury from the reservoir, and in this manner the quantity of fluorine present was measured. The oxygen contained in the residual gases was measured by burning with phosphorus, and the remainder was found to be nitrogen.

Throughout the experiments it was observed that the amount of oxygen present in the current of gases proceeding from the electrolytic tube was always in excess of that due to the air present. After prolonged investigation it was ascertained that this oxygen was not formed by the action of fluorine on moisture in the train of purifiers, but was produced by electrolysis, probably from water absorbed by the solution. Contrary to expectation, this water was not electrolysed away before the fluorine appeared, but persisted throughout the experiment, perhaps owing to the gradual melting of a crystalline solid in the electrolytic tube.

In a recent paper (*Phil. Trans.*, 1905, A, vol. cciv., p. 323), one of the authors has attempted to show that the refractivities of the different members of the same chemical group are related in the ratios of small integers; and it was observed that, if this coincidence were not due to chance, the refractivity of fluorine should bear to that of chlorine the ratio of 1 to 4, which those of neon, oxygen, and nitrogen bear to argon, sulphur, and phosphorus respectively. This prediction has been verified. The refractivity of chlorine for sodium light is 768, or 192×4 ; and that now found for fluorine is 195, a discrepancy of 1½ per cent, which is well within the limits of error of the experiment.

Chemical Oxydases.—G. Baudran.—The author has investigated the action of chlorine, bromine, and iodine on the alkaloids and the toxins.—*Comptes Rendus*, cxli., No. 5.

* Abstract of a Paper read before the Royal Society, June 8, 1905.

THE ABSORPTION SPECTRUM
AND FLUORESCENCE OF MERCURY VAPOUR.*

By W. N. HARTLEY, D.Sc., F.R.S.

HAVING undertaken the investigation of the absorption spectra of metals in a state of vapour, the first substance examined was mercury, and as the results are interesting I have deemed it advisable to make them a separate communication to the Society. F. P. le Roux describes the vapour of mercury as having a bluish colour (*Comptes Rendus*, 1860, vol. li., p. 171), and according to R. J. Strutt, it transmits a feeble steel-blue colour, but the absorption coefficient is small (*Phil. Mag.*, 1902, [6, vol. iv., p. 596; and 1903, vol. vi., p. 76].

Experimental.—The substance to be volatilised was contained in a flask of Heraeus' quartz-glass, with a side tube to the neck from which the metal may be distilled and condensed. To the side tube a water-jacket is fitted, through which a constant stream of water may be passed if necessary. The rays from the condensed spark of a pair of lead-cadmium and tin-cadmium electrodes were passed through the flask and on to a cylindrical condensing lens of quartz which focussed the rays on to the slit of a quartz spectrograph.

The mercury to be used was first purified by distillation. The photographic plates used were various, such as "Rainbow Fast," Warwick plates, Lumière isochromatic, yellow-green sensitive, and Cadett and Neall's "Lightning Spectrum" plates. The mercury vapour in the flask was at a pressure of 847 m.m., the barometer standing at 763 m.m., but the vapour was under a pressure of a column of 84 m.m. of mercury above that of the atmosphere. The temperature was about 360° C., the boiling-point at 760 m.m. being 357°. The volume of the vapour was 31 c.c., and its weight was calculated to be 0.133 gm. The thickness of the layer of vapour was 37 m.m.

Several photographs were taken and particular care was exercised so as to have both ends of the spectrum as well as the central part in accurate focus. The developer used was "imogen sulphite."

The Absorption Spectrum.—The whole rays were transmitted from the red to a point in the ultra-violet where there is a tin-line at λ 2571.67. From there to λ 2526.8 there is a very sharply defined and intense absorption band, somewhat degraded on the side towards the red, beyond that the rays are transmitted with full intensity to a wavelength about 2000.

The Fluorescence.—When the mercury was boiling briskly the whole side of the flask nearest to the spark was lighted up with a green fluorescence; this penetrated about one-third of the space within the flask, and lighted up the interior. The quartz-glass itself was not fluorescent in the slightest degree.

When all the liquid mercury had become converted into vapour, the temperature no doubt rose above that of the boiling mercury, the vapour was quiescent, and the fluorescence ceased. The interior of the flask was then quite dark. By shaking some of the condensed cold mercury down into the flask, the fluorescence was resumed directly the liquid boiled again, but the dropping of cold mercury into the heated vapour caused condensation, and only after the flask had again become filled with the mercury vapour was the fluorescence fully displayed.

When the vapour was rising from the boiling globule of mercury after the cold metal had condensed all within the flask, the vapour could be seen by its fluorescence to undergo condensation in the upper part of the vessel and descend to the hotter space below.

It occurred to me that the actual fluorescence might be associated with oxidation of the vapour, and that it appeared only when such chemical action was taking place, but subsequent observations showed that this could not be the case, because the temperature was above that when

oxidation could occur at the time when the fluorescence was most brilliant, and when it most completely filled the vessel, and also when the mercury vapour had expelled all the air. When the temperature rose above the boiling-point of mercury and excess of liquid mercury and vapour had been expelled from the flask, the fluorescence ceased.

This fact leads to the inference that the fluorescence occurs only between a lower and a higher limit of temperature. What these small differences really are I had no means of determining. Having established the fact that the property of selective absorption is possessed by small quantities of mercury vapour, it was resolved to ascertain whether the band showed itself in solutions of mercury compounds. As a rule the absorption spectra of compounds differ from those of the elements entering into their composition entirely, as in the case of the halogen compounds of the alkali metals; sometimes it is a question of degree, as in the case of the compounds of the rare earth metals, in which similar bands are observed in different salts of the same metal, but in different positions, which vary with the molecular weight of the salts; and there are, still further, other instances where the absorption bands of the solutions are distinctly the properties of the salts, as in the case of the chlorides, bromides, and iodides of cobalt. The salt chosen for examination, because it is the most definite and most soluble, was mercuric chloride. It was examined in cells of 40 m.m. thick, diminishing to 1 m.m. in thickness. The solution contained in the same volume ten times as much mercury as the vapour which filled the flask, or 1.8 grms. of mercuric chloride in 31 c.c. of water; more dilute solutions were examined containing 0.18 gm. and 0.018 gm. No absorption band was visible on any of the spectra photographed, but there was a continuous absorption at the more refrangible end of the spectrum which regularly diminished as the quantity of mercuric chloride in the solution decreased.

Further details are as follows:—

1.8 grms. of mercuric chloride in a cell 40 m.m. thick transmitted all rays to λ 2702, in 1 m.m. to λ 2572; 0.18 gm. in a cell 2 m.m. thick, transmitted all rays to λ 2265; and 0.018 gm. in similar circumstances transmitted very feebly to λ 2145.

The absorption band in the vapour of mercury belongs to the vapour and is accompanied by strong fluorescence between a certain maximum and minimum of temperature lying very near to the boiling-point.

In studying the fluorescence of solutions of organic compounds I have shown that it is necessary to use the ultra-violet rays and quartz apparatus, as it was found that fluorescence was associated very generally with a powerful absorption of rays in the ultra-violet ("Observations on the Origin of Colour and Fluorescence," *Chem. Soc. Trans.*, 1893, vol. lxi., p. 245—256). It is a question still undecided whether the rays absorbed by mercury vapour as shown by the band I have measured, reappear with a lowered refrangibility as yellowish green light in accordance with the law of Stokes.

The spectra were photographed with all due care by my assistant, Mr. Douglas Mellon, A.R.C.Sc.I.

THE PRECIPITATION OF BARIUM BROMIDE
BY HYDROBROMIC ACID.

By NORMAN C. THORNE.

IN former articles from the Kent Chemical Laboratory of Yale University, processes for the separation and determination of certain chlorides, hydrous or anhydrous, by the action of hydrochloric acid have been studied (*Mar. Am. Journ. Sci.*, [3], xliii., 521; Gooch and Havens, *Ibid.*, [4], ii., 416; Havens, *Ibid.*, [4], iv., 111; [4], vi., 45 and 396). The present article deals with the similar separation and determination of barium bromide by the agency of hydrobromic acid.

* A Paper communicated to the Royal Society.

The hydrobromic acid used in the experiments to be described was prepared by dropping from a stoppered funnel liquid bromine into naphthalene dissolved in kerosene, passing the hydrogen evolved through a purifying tower charged in layers with glass-wool and red phosphorus and a water trap, and saturating distilled water with the gas thus purified.

Pure barium bromide was made by dissolving barium chloride in water, precipitating barium carbonate by ammonium carbonate and ammonium hydroxide, washing the precipitate by decantation, and dissolving it in hydrobromic acid. This solution of barium bromide was evaporated to dryness, and the barium bromide thus obtained was used in the following experiments.

In the first series of experiments a weighed amount of the barium bromide was dissolved in the least volume of water, and treated with hydrobromic acid or with a mixture of hydrobromic acid and ether in equal volumes. The liquid was saturated with hydrobromic acid gas, and filtered upon asbestos, and the precipitate washed by a mixture of hydrobromic acid and ether, dried in air-bath or over Bunsen flame, and weighed as BaBr_2 . The details of these experiments are given in Table I.

TABLE I.

BaBr_2 taken. Grm.	HBr. C.c.	HBr and ether. C.c.	BaBr_2 found. Grm.	Error. Grm.
0.2932	30	—	0.2934	+0.0002
0.1264	30	—	0.1260	-0.0004
0.1134	30	—	0.1132	-0.0002
0.1347	—	30	0.1367	+0.0020
0.1040	—	30	0.1035	-0.0005
0.0744	—	20	0.0748	+0.0004
0.1197	—	30	0.1211	+0.0014
0.4327	30	—	0.4345	+0.0018

Considerable difficulty was had in drying the barium bromide so as to obtain a constant weight, and the barium bromide prepared in the manner described did not dissolve completely. The results of these experiments are thereby lacking in uniformity. Presuming that the source of inaccuracy is to be looked for in the formation of an oxybromide, the precipitate in the next experiments, after filtering upon asbestos, was treated with ammonium bromide and then dried over a radiator, at first at a low temperature and finally at a temperature high enough to drive off the ammonium bromide. When the thermometer inside of the radiator showed a temperature of 250°C. , all the ammonium bromide disappeared and left a barium bromide which gave constant results, as shown in Table II.

TABLE II.

BaBr_2 taken. Grm.	HBr and ether. C.c.	BaBr_2 found. Grm.	Error. Grm.
0.1330	30	0.1534	+0.0004
0.1013	30	0.1016	+0.0003
0.2769	30	0.2760	-0.0009
0.2359	30	0.2353	-0.0006
0.1580	30	0.1579	-0.0001
0.2955	30	0.2947	-0.0008
0.2822	30	0.2813	-0.0009
0.1962	30	0.1962	0.0000
0.4127	30	0.4125	-0.0002
0.2751	30	0.2750	-0.0001
0.3181	30	0.3183	+0.0002
0.3049	30	0.3039	-0.0010
0.3754	30	0.3752	-0.0002

These results indicate plainly that barium bromide, prepared in a state of purity and free from oxybromide, may be completely precipitated from solution in water by treatment with a mixture of hydrobromic acid and ether in equal parts and saturation of the liquid with hydrogen bromide.

Some experiments in which precipitation was effected by a mixture of concentrated hydrobromic acid and ether in

equal parts, without saturating with the gas, led to similar results. In these experiments the material weighed out was the crystallised hydrous barium bromide, $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$.

TABLE III.

$\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ taken. Grm.	HBr + ether (1 : 1). C.c.	BaBr_2 found. Grm.	BaBr_2 calculated. Grm.	Error. Grm.
0.2008	30	0.1793	0.1790	+0.0003
0.2041	30	0.1822	0.1820	+0.0002
0.2047	30	0.1821	0.1825	-0.0004
0.2171	30	0.1937	0.1936	+0.0001
0.3101	30	0.2768	0.2765	+0.0003
0.5035	30	0.4496	0.4490	+0.0006
0.5015	30	0.4476	0.4473	+0.0003

The action of hydrobromic acid upon barium chloride was next studied, with or without the presence of salts of calcium and magnesium.

A weighed amount of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, was dissolved in the least volume of water and treated with a mixture of hydrobromic acid and ether in equal volume. The whole solution was saturated with hydrobromic acid gas, filtered upon asbestos, and then, to make sure that no barium oxybromides might be formed, treated with ammonium bromide, dried, and weighed as BaBr_2 .

TABLE IV.

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ taken. Grm.	CaCO_3 . Grm.	MgCO_3 . Grm.	HBr + ether (1 : 1). C.c.	BaBr_2 found. Grm.	Theory as BaBr_2 . Grm.	Error in BaBr_2 . Grm.
0.2253	—	—	30	0.2744	0.2741	+0.0003
0.2088	—	—	30	0.2538	0.2540	-0.0002
0.3273	—	—	30	0.3975	0.3982	-0.0007
0.3177	—	—	30	0.3864	0.3865	-0.0001
0.5041	0.5000	—	30	0.6134	0.6143	-0.0009
0.5083	0.5000	—	30	0.6185	0.6191	0.0006
0.5046	0.5000	—	30	0.6139	0.6136	+0.0003
0.5022	0.5000	—	30	0.6110	0.6104	+0.0006
0.5018	0.5000	—	30	0.6106	0.6108	-0.0002
0.5007	—	0.3000	30	0.6087	0.6092	-0.0005
0.5048	—	0.3000	30	0.6144	0.6142	+0.0002

From these results it is obvious that barium may be separated and determined as the bromide in presence of salts of calcium and magnesium; and it appears also that when the proportion of hydrobromic acid to the barium chloride is that of the experiment and the precipitate ignited with ammonium bromide, the results are in practical accord with those which should be obtained if the precipitate consists entirely of barium bromide.

On the other hand, it appears from the series of experiments given in Table V. that when a sufficiency of hydrochloric acid is added to the water solution of barium bromide, the precipitate falls practically as the chloride.

TABLE V.

$\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ taken. Grm.	HCl used. C.c.	Ether. C.c.	BaCl_2 found. Grm.	BaCl_2 theory. Grm.	Error in BaCl_2 . Grm.
0.2044	25	5	0.1279	0.1277	+0.0002
0.2011	25	5	0.1258	0.1257	+0.0001
0.5021	25	5	0.3138	0.3138	0.0000
0.5037	50	10	0.3148	0.3147	+0.0001
0.5020	25	5	0.3135	0.3137	-0.0002
0.3868	25	5	0.2418	0.2417	+0.0001

So it appears that precipitation is complete in presence of a sufficiency of either acid, and that the precipitate will fall chiefly as the bromide or as the chloride, according to the proportions of hydrobromic acid and hydrochloric acid present.

It was thought a matter of interest in this connection to test the constitution of the precipitates when incomplete precipitation is brought about by addition of one of these acids, the other being present in considerable proportion,

though in amount wholly insufficient to produce by itself precipitation in the volume of water used for solution of the barium salts.

Table VI. is the record of experiments in which 1 grm. of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, was dissolved in water, hydrochloric acid added to incipient precipitation, and then an amount of hydrobromic acid which by itself would produce no precipitation in the water solution. The precipitate was dried and weighed, and the content in bromine determined by the method of Baubigny and Rivals (*Comptes Rendus*, cxcv., 527, 607).

TABLE VI.

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ taken.	Water for solution.	HBr added.	HCl added.	Pre- cipitate.	Bromine in pre- cipitate.	BaBr_2 in precipi- tate.
Grm.	C.c.	C.c.	C.c.	Grm.	Grm.	Grm.
1	30	3	22	0.5037*	0.0129	0.0240
1	42	5	31	0.6241†	0.0141	0.0263
1	40	5	30	0.6338†	0.0202	0.0375

* Dried three months in desiccator over sulphuric acid.

† Dried six hours at 80° and twelve hours in desiccator over sulphuric acid.

The meaning of these results seems to be that the precipitation of the bromide is induced by the action of the hydrogen chloride upon the solvent, water. The production of free bromine ions and barium ions to the amount of the solubility product of barium bromide in water is, under the conditions, an impossibility. It is to be admitted, it seems highly probable that precipitation of barium chloride is likewise conditioned by the action of the hydrogen chloride upon the solvent.

It has been customary on the part of some to explain the similar precipitation of other chlorides soluble in water, like sodium chloride, by large amounts of hydrochloric acid, upon the assumption that insolubility is due to increased concentration of the chlorine ions, and such processes have been held to be typical of processes in which precipitation is affected by concentration of the free ions. It seems more probable, however, that it is the action of the hydrogen chloride upon the solvent which is the effective thing in such precipitations, as in the precipitation of barium bromide, after addition of hydrochloric acid, by an amount of hydrobromic acid wholly insufficient to cause precipitation in the water solution.

I wish to express my thanks to Prof. Gooch for suggestions and advice given during the progress of this work.—*American Journal of Science*, xviii., p. 441.

NOTICES OF BOOKS.

A Class-book of Elementary Chemistry. By W. W. FISHER, M.A., F.C.S. Fifth Edition, Revised and Enlarged. Oxford: Clarendon Press. 1905.

NUMEROUS important additions have been made to this class-book, which appears to contain a good grounding for the student of elementary chemistry. The plan of the first edition is followed, but the matter has been carefully brought up to date, in accordance with our latest knowledge of the developments of the science. A new feature is the addition of several chapters on organic chemistry. In these the properties and methods of preparation of various typical compounds—such as alcohol, oxalic acid, toluene—are described, and simple constitutional and structural formulæ are also discussed. The space devoted to organic chemistry is only a very small part of the whole, with the result that the treatment is rather too sketchy to be of any real use to the student, but in other respects the book appears to be a very fair specimen of the descriptive class of books on elementary chemistry.

Dispensing Made Easy. By WM. G. SUTHERLAND, M.B. (Aberd.). Second Edition. Bristol: John Wright and Co. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1905.

This little book well deserves the favourable reception accorded to it, and we are not surprised to learn that it has already run through its first edition. The second edition has been made rather fuller than the first in the way of additional formulæ, thoroughly tested by experience, and has been revised, so that it provides a most handy and reliable practical guide from which both the dispenser and the medical man can glean much useful information. The book contains, in a very concise form, a great variety of formulæ, practical hints on dispensing (specially with a view to ensuring the utmost economy both of money and time), and also ample space for memoranda and private formulæ.

Twenty-eighth Annual Report of the Connecticut Agricultural Experiment Station. For the Year ending October 31, 1904. New Haven, Conn.: The Tuttle, Morehouse, and Taylor Company. 1905.

A LARGE amount of useful matter is contained in this report, which gives a full account of the valuable work done by the Connecticut Agricultural Station. The report is sent free to any citizen of the State who applies for it, and, under certain circumstances, free analyses of fertilisers, foods, &c., are made for the benefit of the citizens. The report contains very valuable information concerning the price, composition, and actual value of large numbers of manures and commercial feeding-stuffs, the results in the case of the latter having been already published as a Bulletin in January of this year. The standards of purity for food products adopted by the Station are given at length, and the results of the analyses of some hundreds of substances of all kinds are tabulated. As the dealer and brand are in all cases stated in full, the citizen of Connecticut may very readily avoid purchasing adulterated or inferior foods of any description. Moreover, the analytical chemist will find in the book some useful hints as to methods of analysis, which experience has shown are the most convenient and accurate. Besides these chemical reports, the book includes the State Entomologist's Bulletin, containing notes on the identification and destruction of injurious insects, and also the results so far obtained during the mosquito investigation; and the State Botanist describes his researches on various blights; these two sections being copiously illustrated by plates.

Buletinul Societatii de Stiinte din Bucuresti, Romania. ("Bulletin of the Scientific Society of Bucharest, Romania"). Vol. XIV. Bucuresti: Imprimeria Statului. 1905.

THIS volume contains the minutes of two meetings of the flourishing Scientific Society of Bucharest, as well as several papers—some of which are written in French—on mathematical, biological, and other subjects. One communication only deals with a chemical subject, namely, a paper by Dr. Adriano Ostrogovich on methyl diamino-triazine, which contains a very complete account of the thorough investigation of the properties and reactions of the triazine and its chief derivatives.

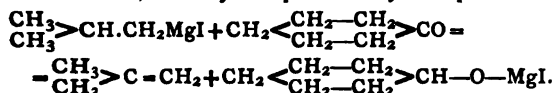
Simple Method of Preparing Halogen Alkyls.—R. F. Weinland and Karl Schmid.—Neutral esters of sulphuric acid are formed by the action of silver sulphate upon alkyl halogens. The reverse reaction, i.e., the formation of alkyl haloids from the dialkyl sulphate and metallic haloid, takes place readily in aqueous solution as follows:— $\text{SO}_4(\text{CH}_3)_2 + \text{KI} = \text{CH}_3\text{I} + \text{SO}_4\text{K}(\text{CH}_3)$. This method is very simple, and the alkyl halogens are obtained by it in the pure state, the yield being almost quantitative. Various methyl haloids may be prepared by this method, and also the ethyl compounds, but in the case of the latter the reaction takes place more slowly.—*Ber.*, xxxviii., No. 10.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 5, July 31, 1905.

A Secondary Reaction of Halogen Organo-magnesium Compounds.—Paul Sabatier and A. Mailhe.—The authors observe certain secondary reactions taking place when the aromatic or cyclo-forminic acetones react on various organo-magnesium halogen compounds. In the case of isobutyl and its derivatives this reaction is most marked, and may be represented by the equation—

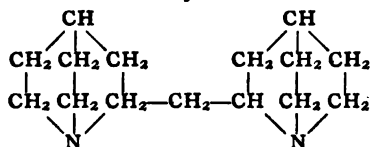


This reaction is reduced to a minimum when the temperature is very low.

State of Matter when nearing its Critical-point.—Gabriel Bertrand and Jean Lecarme.—The author's experiments show that when nearing the critical-point, and also at a temperature rather higher than this point, matter can exist at the same time in a liquid and gaseous state. In the case of a single substance there is present in the tube, not only a layer of pure liquid and a layer of pure vapour, but a layer of solution of vapour in liquid and a solution of liquid in vapour. This latter is doubtless relatively less concentrated than the former. The solubility of the vapour in the liquid, and the dissolving power of this vapour for the liquid, increases with the temperature and pressure. When the critical temperature is reached, the density of the two layers becomes identical. But it is quite perceptible that, at a decidedly higher temperature, a portion of the matter may still retain its liquid state.

Different Stages of Oxidation of Aluminium Powder.—M. Kohn-Abrest.—When aluminium powder is heated in a boat in contact with air to accurately measured temperatures and for accurately determined periods of time, the author finds that the quantities of oxygen taken up by the powder vary according to the method of operation. The velocity of the current of air exercises a most marked influence on appearance of the metal and on the magnitude of the oxidation.

Constitution of Spartein.—Charles Moureu and Amand Valeur.—The authors make a series of experiments to discover the constitution of spartein, and find it to be represented by the following formula, in which each atom of nitrogen is united to an asymmetric carbon:—



This formula, recognised by the presence of two bicyclic nitrogen radicles in symmetric position, agrees perfectly with the facts revealed by the researches of MM. Willstätter and Marx and MM. Herzog and Meyer.

Variations of the Basic Function in Chromium Salts.—Albert Colson.—In order to explain the inactivity of a normally prepared chromic pentasulphate, the author had to admit that the green oxide precipitated from chrome alum is a condensed oxide due to loss of water, $2\text{Cr}(\text{OH})_3 = \text{H}_2\text{O} + \text{O} \cdot \text{Cr}_2(\text{OH})_4$. If this is the case, a weak monobasic acid should give with this base a derivative of the form $\text{O} \cdot \text{Cr}_2\text{X}_6$, and not the sesqui-salt Cr_2X_6 . This is what happens in reality when 1 mol. of this oxide is left to

digest with 6 mols. of dilute cold acetic acid. A violet solution is obtained, having the appearance of a normal acetate, but which in reality contains one-third part of acetic acid in the free state. The author proves this fact by several experiments.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 10, 1905.

Crystalline Form of Sodium Formaldehyde Sulphoxylic Acid (Rongalite C).—A. Osann.—This salt, the first derivative of a new acid H_2SO_2 , corresponding to an oxide SO , is employed in calico printing. The constitutional formula is probably $\text{CH}_2 < \begin{array}{c} \text{OH} \\ | \\ \text{O} \cdot \text{SO} \cdot \text{H} \end{array}$. The sodium salt is characterised by a remarkable power of crystallisation. Perfectly formed crystals, weighing 400 grms. may be obtained without difficulty, but unfortunately the substance is strongly hygroscopic, so that the measurements of the crystals are affected by the moistness of their surfaces. The substance is very soluble in water, 1 litre of cold water dissolving 500 to 600 grms. of rongalite. The crystalline system is rhombic-holohedral, the ratios of the axes being $a : b : c = 0.8421 : 1 : 0.6783$.

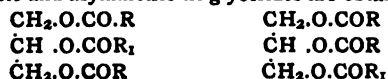
Influence of Silver Nitrate upon the Solubility of Silver Nitrite.—Alex. Naumann and Adolf Rücker.—The authors find that the influence of silver nitrate upon the solubility of the nitrite is not that deduced from van't Hoff's equation expressing the influence of similar ions upon solubility. Even taking into account the incomplete dissociation of the silver nitrate added, a considerable discrepancy still exists. It might be supposed that the formation of double salts is responsible for this discrepancy, but it is highly improbable that such formation would occur to exactly the same extent in all the cases investigated which do not follow the equation, and, moreover, when the process of crystallisation of the mixtures of silver nitrite and nitrate is observed under the microscope, no third salt can be detected. Thus, although the theory of electrolytic dissociation furnishes on the whole a satisfactory explanation of the processes observed, the actual relations found experimentally exhibit discrepancies which have not yet been explained.

Action of Glacial Acetic - hydriodic Acid on Quinones.—K. Lagodzinski.—The author finds that if anthraquinone is suspended in glacial acetic acid, the mixture heated to boiling, and hydriodic acid of specific gravity 1.70 added, the light yellow suspension becomes dark brown, and the anthraquinone goes into solution. On cooling, brown glittering needles separate out. The author has examined several derivatives of anthraquinone, such as alizarin, quinizarin, &c., to see if they also give this reaction, and has found that all these substances, which are difficultly soluble in acetic acid alone, on addition of hydriodic acid, readily give dark brown solutions. Phenanthraquinone and benzil both react similarly with glacial acetic acid and hydriodic acid. The compounds formed have apparently a complicated structure, and in some cases it may be proved that the hydriodic acid takes part in the reaction.

Action of Diazo Compounds upon Primary Aliphatic Amines.—Otto Dimroth.—When diazo compounds react with amines, first of all one molecule of diazonium salt reacts with one molecule of aliphatic amine and triazenes are formed, which are characterised by yielding nitrogen with acids in the cold. The tendency to unite with two molecules of diazo compound is far more strongly developed in the case of the aliphatic amines than with the aromatic bases, and even if the amine is used in considerable excess a large amount of bis-diazo-amine compound is formed. But under suitable experimental conditions, viz., if the triazene is at once removed from the solution, it is possible to check the reaction so that only mono-diazo-amino compound is formed.

Halogen Compounds of Palladium.—A. Gutbier and A. Krell.—In the course of experiments aiming at the determination of the atomic weight of palladium, the authors have prepared some new double salts of palladium chloride and bromide, and have also for the first time obtained derivatives of palladic bromide. They find that ammonium palladium chloride possesses the formula $(\text{NH}_4)_2\text{PdCl}_6$, and thus does not contain a molecule of water of crystallisation; they have obtained the chloropalladates of caesium and rubidium in the crystalline form, and have converted them into the corresponding derivatives of palladic chloride by treatment of their aqueous solution with chlorine gas. Several double salts of palladium bromide are obtained by the cautious evaporation of mixed solutions of palladium bromide with other bromides, and by the action of bromine vapour upon their aqueous solution the corresponding derivatives of palladic bromide are obtained. Neither palladic bromide nor chloride can be obtained in the pure state. The general formula of the double bromides is Me_2PdBr_6 . They are stable in air, difficultly soluble in cold water, and are decomposed by hot water, bromine being liberated. Concentrated ammonia reduces them to the corresponding bromopalladate, which dissolves in excess of ammonia, and can be converted into palladosamine bromide. All these compounds when cautiously heated in a current of hydrogen give up the whole of their halogen, forming halogen acid.

Synthesis of Fats.—Ad. Grün.—The author has found that it is often best to prepare the glycerides of higher fatty acids by allowing the solution of the fatty acid in concentrated sulphuric acid to act upon the sulphuric acid ester of the glycerin or upon the chlorhydrine. The esterification of glycerin by sulphuric acid (even when great excess of acid is used) ceases with the formation of glycerin disulphuric acid, $\text{C}_3\text{H}_5(\text{OH})(\text{OSO}_3\text{H})_2$, and when organic acids act upon this compound diglycerides are formed, containing two acyl groups. The reaction proceeds very rapidly at a relatively low temperature, and the yield is good, but cannot be made to exceed 70–80 per cent of the theoretical, the action being reversible. No mono- or tri-glycerides appear to be formed, nor were any by-products obtained. Apparently only the two primary hydroxyl groups of the glycerin are esterified, while in α -chlorhydrine the primary and secondary groups are equally easily acted upon, yielding both $\alpha\alpha$ - and $\alpha\beta$ -diglycerides. If the hydroxyl or chlorine is replaced by a fatty acid residue, which differs from the acyl already contained in the molecule, structuro-isomeric pairs of symmetric and asymmetric tri-glycerides are obtained:—



In the author's opinion it must be possible to split up the latter tri-glyceride into optically active components.

MISCELLANEOUS.

The Iron and Steel Institute.—(President: R. A. HADFIELD.—The following is a revised list of the Papers that have been offered for reading at the Sheffield Meeting, September 26–29, 1905:—

- "On the Wear of Steel Rails on Bridges." By Thomas Andrews, F.R.S. (Wortley).
- "On the Metallurgical Department of Sheffield University." By Prof. J. O. Arnold (Sheffield).
- "On the Thermal Transformation of Carbon Steels." By Prof. J. O. Arnold and A. McWilliam (Sheffield).
- "On the Nature of Troostite." By Dr. Carl Benedicks (Uppsala).
- "On the Transformations of Nickel Steels." By L. Dumas (Paris).
- "On Steel for Motor-car Construction, and on Vanadium Steels." By L. Guillet (Paris).

"On the Occurrence of Copper, Cobalt, and Nickel in American Pig Irons." By Prof. E. D. Campbell (Ann Arbor, Michigan).

"On the Presence of Greenish-coloured Markings in the Fractured Surface of Test Pieces." By Captain H. G. Howorth, R.A. (Sheffield).

"On Over-heated Steel." By Arthur W. Richards (Grange-town) and J. E. Stead, F.R.S. (Member of Council).

"On Segregation in Steel Ingots." By B. Talbot (Middlesbrough).

"On a Manipulator for Steel Bars." By Douglas Upton (Jarrow).

"On the Influence of Carbon on Nickel and Iron." By George B. Waterhouse (New York).

Members who intend to take part in the discussion will, on notifying such intention to the Secretary, have copies of the papers forwarded to them a week in advance, as far as that may be possible. The Housing Committee of the Sheffield Reception Committee are making arrangements for those members who have stated, on their reply forms, their intention of being present. In view, however, of the unprecedentedly large number of members and ladies who have intimated their intention of attending the meeting, difficulty has been experienced in providing accommodation; and it has, with regret, been found impossible to avoid limiting to some extent the number of ladies. Members are therefore informed that invitations cannot be extended to more than one lady accompanying each member. Full particulars of the meeting may be obtained of Mr. BENNETT H. BROUGH, Secretary, 28, Victoria Street, London, S.W.

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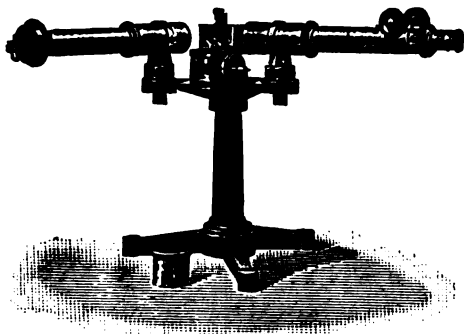
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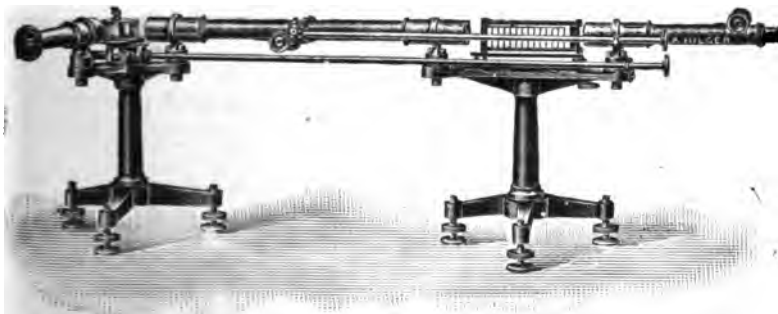


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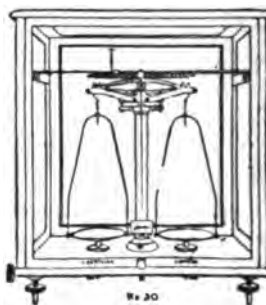
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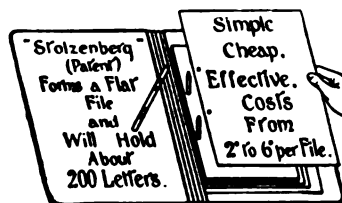
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THE CHEMICAL NEWS.

VOL. XCH., No. 2389.

ON THE INFLUENCE OF COLLISIONS AND OF THE MOTION OF MOLECULES IN THE LINE OF SIGHT, UPON THE CONSTITUTION OF A SPECTRUM LINE.*

By Lord RAYLEIGH, O.M., F.R.S.

APART from the above and other causes of disturbance, a line in the spectrum of a radiating gas would be infinitely narrow. A good many years ago (*Phil. Mag.*, 1889, vol. xxvii., p. 298; *Scientific Papers*, vol. iii., p. 258), in connection with some estimates by Ebert, I investigated the widening of a line in consequence of the motion of molecules in the line of sight, taking as a basis Maxwell's well-known law respecting the distribution of velocities among colliding molecules, and I calculated the number of interference-bands to be expected, upon a certain supposition as to the degree of contrast between dark and bright parts necessary for visibility. In this investigation no regard was paid to the collisions; the vibrations issuing from each molecule being supposed to be maintained with complete regularity for an indefinite time.

Although little is known with certainty respecting the genesis of radiation, it has long been thought that collisions act as another source of disturbance. The vibrations of a molecule are supposed to remain undisturbed while a free path is described, but to be liable to sudden and arbitrary alteration of phase and amplitude when another molecule is encountered. A limitation in the number of vibrations executed with regularity necessarily implies a certain indeterminateness in the frequency, that is a dilatation of the spectrum line. In its nature this effect is independent of the Doppler effect—for example, it will be diminished relatively to the latter if the molecules are smaller; but the problem naturally arises of calculating the conjoint action of both causes upon the constitution of a spectrum line. This is the question considered by Mr. C. Godfrey in an interesting paper ("On the Application of Fourier's Double Integrals to Optical Problems," *Phil. Trans.*, A, 1899, vol. cxcv., p. 329), upon which it is the principal object of the present note to comment. The formulæ at which he arrives are somewhat complicated, and they are discussed only in the case in which the density of the gas is reduced without limit. According to my view this should cause the influence of the collisions to disappear, so that the results should coincide with those already referred to where the collisions were disregarded from the outset. Nevertheless, the results of the two calculations differ by 10 per cent, that of Mr. Godfrey giving a narrower spectrum line than the other.

The difference of 10 per cent is not of much importance in itself, but a discrepancy of this kind involves a subject in a cloud of doubt, which it is desirable, if possible, to dissipate. Mr. Godfrey himself characterises the discrepancy as paradoxical, and advances some considerations towards the elucidation of it. I have a strong feeling, which I think I expressed at the time, that the 10 per cent correction is inadmissible, and that there should be no ambiguity or discontinuity in passing to the limit of free paths infinitely long. In connection with some other work I have recently resumed the consideration of the question, and I am disposed to think that Mr. Godfrey's calculation involves an error respecting the way in which the various free paths are averaged.

The first question is as to the character of the spectrum line corresponding to a regular vibration which extends over a finite interval of time. As the energy lying between

the limits n and $n + dn$ of frequency (or rather inverse wave-length), Mr. Godfrey finds from Fourier's theorem—

$$\frac{\sin^2 \pi r n}{n^2} dn \dots \dots \dots (1),$$

r denoting the finite length of the train of waves, and n being measured from that value which would be dominant if r were infinitely long. For the total energy of all wave-lengths we have—

$$\int_{-\infty}^{+\infty} \frac{\sin^2 \pi r n}{n^2} dn = \pi^2 r \dots \dots \dots (2).$$

That the total energy should be proportional to r is what we would expect. The maximum coefficient in (1) occurs, of course, when $n = 0$, and is proportional to r^2 ; once proportional to r on account of the greater total energy as given in (2), and again on account of the greater condensation of the spectrum as r increases. Expression (1) may be taken to represent the spectrum of the radiation from a single molecule which describes in a given direction and with a given velocity a free path proportional to r . If there be N independent molecules answering to this description, N may be introduced as a factor into (1). From this expression Mr. Godfrey proceeds to investigate the spectrum corresponding to the aggregate radiation of the gas, integrating first for the different lengths (r) of parallel free paths described with constant velocity, and afterwards for the various component velocities across and in the line of sight, the latter giving rise to the Doppler effect. It is with the first of these integrations that I am more particularly concerned.

In order to effect it, we need to know the probabilities of the various length of free path described with given velocity. "Now, Tait has shown that, of all atoms moving with velocity v , a fraction $e^{-f/\rho}$ penetrates unchecked to distance ρ where f is a function of v and of the permanent data of the gas). From this we see that, of molecules moving with velocity v , a fraction $f e^{-f/\rho} d\rho$ have free paths between ρ and $\rho + d\rho$. Now, such a molecule will emit an undisturbed train of waves of length between r and $r + dr$, where $r = \rho \cdot V/v$, and V is the velocity of light. Hence, of all molecules moving with velocity v , a fraction $(f v/V) e^{-v/r/V}$ will give free paths between r and $r + dr$. Returning to the expression (1) for the energy of a single train of length r , we see that with the aggregates of molecules now under consideration (definite thwart and line-of-sight velocities) we have for n a proportion of energy—

$$\frac{f v}{n^2 V} \int_0^\infty e^{-v/r/V} \sin^2 \pi n r \cdot dr,$$

or, on effecting the integration,—

$$\frac{2\pi^2}{4\pi^2 n^2 + v^2 f^2/V^2} \dots \dots \dots (3).*$$

The next steps are integrations over the various velocities, but it is not necessary to follow them here in detail, inasmuch as the objection which I have to take arises already. It appears to me that what we are concerned with is not the momentary distribution of free paths among the molecules which are describing them, but rather the statistics of the various free paths (described with velocity v) which occur in a relatively long time. During this time various free paths occur with frequencies dependent on the lengths. Fix the attention on two of these, one long and one short. They present themselves in certain relative numbers, or say in a certain proportion, and it is with this proportion that we have to do. The other procedure takes, as it were, an instantaneous view of the system, and, surveying the molecules, inquires what proportion of them are pursuing free paths of the two lengths under contemplation. It is not difficult to recognise that this is a different question. Of the paths which are described in a given period of time, an instantaneous survey is more likely to hit upon a long

* Mr. Godfrey's expression (iii.) differs somewhat from (3). A $4\pi^2$ appears to have been temporarily dropped, but this is not material for my present purpose.

* A Paper communicated to the Royal Society.

one than upon a short one. Thus Mr. Godfrey's integration favours unduly the long paths.

The above consideration indicates that we ought to divide by r previously to integration, that is, evaluate—

$$\frac{fv}{n^2V} \int_0^\infty r^{-1} e^{-vr/V} \sin^2 n\pi r \cdot dr \quad (4).$$

If we write—

$$\int_0^\infty r^{-1} e^{-cr} \sin^2 ar \, dr = y,$$

we find—

$$\frac{dy}{da} = \frac{2a}{4a^2 + c^2},$$

and—

$$y = \frac{1}{2} \log \frac{4a^2 + c^2}{c^2}.$$

Hence—

$$(4) = \frac{fv}{4n^2V} \log \left\{ 1 + \frac{4n^2\pi^2V^2}{v^2f^2} \right\} \quad (5),$$

in place of (3).

It must be remarked, however, that an over-valuation of long paths relatively to shorter ones which all correspond to the same velocity, would not of itself explain the 10 per cent discrepancy; for, when the gas is infinitely rare, all the paths must be considered to be infinitely long, and then the proportion of relatively longer and shorter paths becomes a matter of indifference. In fact (3) should give the correct result in the limit ($f=0$), even though it be of erroneous form as respects n , provided a suitable function of f and v be introduced as a factor. If we integrate (3) as it stands with respect to n between the limits $-\infty$ and $+\infty$, we obtain—

$$\frac{2\pi^2V}{vf} \quad (6).$$

But this should certainly be independent of f . I think that if we introduce the factor vf into (3), Mr. Godfrey's analysis would then lead to the same result as is obtained by neglecting the influence of collisions *ab initio*.

It may be convenient to recite the constitution and visibility of a spectrum line according to the simple theory, where the Doppler effect is alone regarded. If ξ be the velocity of a molecule in the line of sight, the number of molecules whose velocities in this direction lie between ξ and $\xi + d\xi$ is, by Maxwell's theory,—

$$e^{-h\xi^2/d\xi} \quad (7).$$

According to Doppler's principle the reciprocal wavelength of the light received from these molecules is changed from Λ^{-1} , corresponding to $\xi=0$, to $\Lambda^{-1}(1+\xi/V)$, V being the velocity of light. If x denotes the variation of reciprocal wave-length, $x = \Lambda^{-1}\xi/V$, and the distribution of light in the dilated spectrum line may be taken to be—

$$e^{-hV^2\Lambda^2x^2} \quad (8).$$

When this light forms interference-bands with relative retardation D , the "visibility" according to Michelson's reckoning is expressed by—

$$\int_{-\infty}^{+\infty} e^{-hV^2\Lambda^2x^2} \cos(2\pi Dx) \, dx \div \int_{-\infty}^{+\infty} e^{-hV^2\Lambda^2x^2} \, dx;$$

that is,—

$$e^{-\frac{\pi^2 D^2}{hV^2\Lambda^2}} \quad (9).$$

If v be the velocity of mean square, on which the pressure of the gas depends,—

$$v^2 = \frac{3}{2h} \quad (10).$$

In terms of v the exponent in (8) is—

$$-\frac{3V^2\Lambda^2x^2}{2v^2} \quad (11),$$

and that in (9) is—

$$-\frac{2\pi^2v^2D^2}{3V^2\Lambda^2} \quad (12).$$

ESTIMATION OF OIL IN WATER FROM CONDENSING ENGINES.

By J. McFARLANE and J. MEARS.

If the oil exceeds 0.4 grain per gallon, use 1 litre for the determination; if below 0.4 grain per gallon, use 2 litres.

Add to 2 litres of the water contained in a 2½-litre flask 5 c.c. of the "ferric chloride" solution and heat up nearly to boiling; then add ammonia in excess, to precipitate the iron (which precipitate contains all the oil), and boil for two minutes.

Allow to stand a few minutes and filter through a 15 c.m. filter-paper which has been previously extracted with ether, washing the precipitate on to the paper with hot water, and washing three or four times with hot water. Then dry the filter and precipitate in the water oven at 100° C. and, when dry, extract with ether in the Soxhlet in the usual way, evaporate the ether extract, and weigh the remaining oil.

Ferric Chloride Solution.—Ten grms. of iron dissolved in 200 c.c. of hydrochloric acid, oxidised with HNO_3 , and made up to 1 litre.

NOTES ON THE ANALYSIS OF DOLOMITE.

By NICHOLAS KNIGHT.

It is well known to analysts that, other things being equal, the simpler and more direct the methods of analysis the better. There is not only a saving of time, but the possibility of loss by the complexity of the processes is diminished. This applies to the trained and experienced chemist, and with especial force to the amateur who is beginning his course in quantitative analysis. The chemical work of the ordinary college student is of necessity so interrupted by his other studies that the direct and simple methods are of peculiar interest and value to him.

In connection with this subject, attention is called to the analysis of dolomite as outlined in the excellent work on Quantitative Analysis by Clowes and Coleman. The writer values the work very highly, and takes pleasure in acknowledging his indebtedness to it in his teaching. We have found that some of the steps directed to be taken in the analysis of this rock can just as well be omitted. The object of this paper is to show that such is the case.

The rock that was studied abounds in Eastern Iowa and in many other parts of the United States. It belongs to the Niagara period, and it is nearly a pure dolomite. It is used extensively as a building stone and in the manufacture of quicklime.

1. *The Insoluble Residue, mainly or wholly Silica, in the Specimens examined.*—According to Clowes and Coleman, after dissolving 1½ grms. of the substance in dilute hydrochloric acid, a little strong nitric acid is added, and the whole is evaporated to dryness on the water-bath in a porcelain evaporating dish. The dish is then heated for an hour in the air-bath to 150° "to convert the silica into the anhydrous insoluble condition." The dish is then allowed to cool, and its contents are heated with a small quantity of strong hydrochloric acid, which dissolves everything except silica and clay. This is filtered and determined.

2. *Another Method for the Insoluble Residue.*—A gm. of the fine powder was weighed into a small beaker, and a little dilute hydrochloric acid was added. The contents of the beaker were gently heated to the boiling-point; the insoluble residue was filtered off, and its weight determined. The following results were obtained:—

Method 1.	Method 2.
0.94 per cent	0.938 per cent
0.87 "	0.87 "
0.89 "	0.88 "

In cases of this kind Method 2 is much shorter, and gives practically the same results as the other. It is therefore to be preferred.

3. *To Determine the Iron and Alumina, Fe_2O_3 and Al_2O_3 .*—(A). About 2 grms. ammonium chloride and a little fuming nitric acid are added to the filtrate from the insoluble residue. This is heated to boiling, and the iron and aluminium hydroxides are precipitated with a small excess of ammonium hydrate. The precipitate is quickly filtered off by the use of a pump well washed in hot water, dried, and its weight determined.

(B). According to Clowes and Coleman it is necessary to re-dissolve the well washed precipitate of iron and aluminium hydroxides with hydrochloric acid and precipitate again with ammonia. This double precipitation is necessary, they say, in order to separate completely the small amount of calcium which is precipitated with the iron and aluminium hydroxides. It is not stated why the calcium is precipitated, but all or nearly all ammonia contains more or less ammonium carbonate. This would precipitate the calcium. Yet, while the solution to which the ammonia is added remains acid, ammonium chloride would result from the carbonate, and no calcium could be precipitated. Moreover, the iron present in the solution serves as an indicator by its change of colour, so that no more than a drop or two of ammonia in excess is necessary to be added. The small amount of calcium carbonate that this excess would precipitate, insoluble as it is, is doubtless removed by washing the precipitate sufficiently with hot water. At any rate, the experiment was made a number of times of dissolving the precipitate of iron and aluminium hydroxides with hydrochloric acid and re-precipitating with ammonia. No trace of calcium nor magnesium could be found in the filtrates.

The results obtained by Methods A and B were as follows:—

Al_2O_3 and Fe_2O_3 (per cent).

A.	B.
0.59	0.54
0.55	0.51
0.51	0.48

The calcium was determined by heating the filtrate from the iron and aluminium hydroxides to boiling, and precipitating with the smallest possible excess of ammonium oxalate. Enough of the reagent must be added to insure complete precipitation. This precipitates a small amount of magnesium with the calcium. It is therefore necessary to dissolve the precipitate in warm dilute hydrochloric acid and re-precipitate the calcium with ammonia. This leaves the magnesium in solution.

The two filtrates containing magnesium are united and concentrated to a volume of about 200 c.c. on the water-bath. No difficulty was then experienced in precipitating the magnesium with disodium phosphate and ammonia.

The complete analysis of the specimen resulted as follows:—

	Per cent.
Insoluble residue, mainly SiO_2	0.87
Fe_2O_3 and Al_2O_3	0.48
CaCO_3	53.10
MgCO_3	45.55
	100.00

The carbon dioxide was determined by the Bunsen method.

Clowes and Coleman would precipitate the calcium with a considerable excess of ammonium oxalate, and then evaporate the filtrate from the calcium to dryness, heating further to remove the ammonium salts. "This removal of ammonium salts is necessary, since they prevent the complete precipitation of magnesium." This has not been our experience. A gm. of the original powder will give as accurate results as a gm. and a-half. Some of the precipitates are so large as to be unwieldy with the larger amount of substance.

A second specimen of the dolomite slightly different in composition from the preceding was also studied. The insoluble residue, which was mostly silica, was determined as follows:—

	Method 1.	Method 2.
SiO_2 (per cent)	0.81	0.95
	—	0.88

The Iron and Aluminium Oxides.

	Method A.	Method B.
Fe_2O_3 and Al_2O_3 (per cent)	2.28	2.43
	—	2.36
	—	2.28
	—	2.26

On dissolving the iron and alumina with hydrochloric acid, and re-precipitating with ammonia, no trace of calcium or magnesium could be found in the filtrate.

The analysis of a similar specimen resulted as follows:—

	Per cent.
CaCO_3	53.87
MgCO_3	49.59
Fe_2O_3 and Al_2O_3	2.43
SiO_2	0.95
	99.84

The author acknowledges his indebtedness to Frances Benson and H. O. Cheney for carrying on the experiments described in this paper.

Cornell College, August 8, 1905.

THE DETERMINATION OF THE WAVE-LENGTHS IN THE SPECTRUM OF GIESEL'S EMANIUM.

By J. HARTMANN.

In my earlier communication on the spectrum of emanium light I expressed the hope that, with a more powerful spectrograph, I should be able to determine more accurately the position of the exceedingly faint lines in the yellow and green parts of the spectrum (*Physikal. Zeit.*, 1904, v., 570). I have now concluded this research, using Giesel's preparation, which has preserved its luminosity unimpaired, and will now describe the result of my measurements.

The spectrograph, S, used for the experiments was most kindly placed at my disposal by Prof. v. Drygalski from the stock of the German South Pole Expedition, for which I had prepared the apparatus. The spectrograph, constructed according to Prof. Scheiner's directions, contains a flint-glass prism of 60° and, as objectives of collimator and camera, two Zeiss's planars of 30 m.m. aperture and 110 m.m. focal length. It thus probably reaches the extreme limit as regards the strength of the light, and is well suited for taking faint spectra; the linear extension of the spectra is indeed so small that, especially in the less refrangible parts of the spectrum, the wave-lengths can be measured only to 1 A.U., which, however, is quite accurate enough in the investigation of such faint spectra. As the apparatus, on account of the quantities of glass in its objectives, absorbs the short wave-lengths strongly, in the investigation of the ultra-violet part of the spectrum I used a very powerful quartz spectrograph, which has recently been described in the *Zeitschrift für Instrumentenkunde* (1905, xxv., 161). The experiments performed with this apparatus are marked Q.

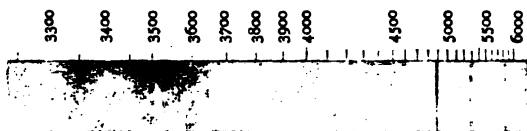
The wave-lengths refer to the measurement of the following six plates:—

Plate S 23	135 hours illumination.
" S 24	191 " "
" S 25	170 " "
" Q 100	36 " "
" Q 101	24 " "
" Q 102	48 " "

A.	F.	Description.
3250		Commencement of a continuous band.
3560		Maximum intensity of the band.
3810		End of the band.
4070		Commencement of a feebler continuous band.
4340		Maximum of the band.
4720		End of the band.
4137	+3 A.U.	Very faint, fine line.
4743	4	Very faint, fine line.
4885.4	0.1	Principal line; breadth from about 4879—4894.
5287	10	Fainter, very broad line; specially indistinct towards the red, from about 5245—5320. It is probably a double line, the stronger component of which lies at 5272 and the fainter at 5306.
5704	10	Exceedingly faint line, the existence of which is not quite certain.
5838	10	Broad, indistinct line, somewhat fainter than 5287; breadth from 5800 to 5900.

The wave-length previously given by me for the principal line, 4885.4, was completely confirmed by the new measurements, but, on the other hand, the wave-length of the last line, which was previously measured only very roughly, was considerably altered. Moreover, the new experiments have proved with additional certainty the existence of the two lines 4137 and 4743, while the existence of the line 5704, only shown on one plate, still remains uncertain. Under F is given in the table the probable error in the wave lengths.

The accompanying figure shows the whole image of the spectrum (negative).



As regards the interpretation of this spectrum, this could be sought in two directions, according to my opinion which I have already expressed. Firstly, we might assume that a gas mechanically retained by the substance was excited to luminescence by the radiation of the emanation, just as Sir William and Lady Huggins found the band spectrum of nitrogen in the light of radium preparations (*Proc. Roy. Soc.*, 1903, lxxii., 196 and 409). My repetitions of the Huggins' researches have, however, hitherto only given a negative result, for with two different radium preparations, both in air and in hydrogen, I only obtained a continuous spectrum and no trace of a gas spectrum.

Secondly, we might assume that traces of a rare earth held in solid solution in the substance were brought to fluorescence by the radiation. This last supposition has now actually been confirmed by Giesel (*Berichte*, 1905, xxxviii., 775), who has succeeded in producing a fluorescence spectrum, very similar to the spectrum of emanium, by dissolving small quantities of didymium in lanthanum chloride, which also forms the greater part of his emanium preparation.

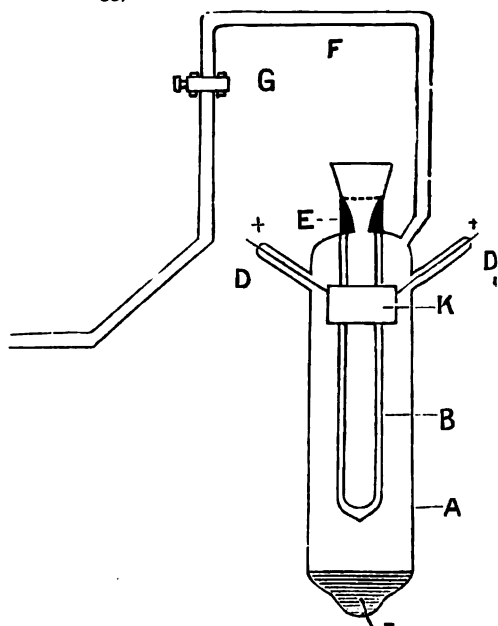
Whether the emanium spectrum is perfectly identical with the didymium spectrum can only be determined by a more accurate measurement of the latter, which presents no difficulty of any kind taking into account the considerably greater strength of light which this possesses on excitation with cathode rays. To render this comparison with the didymium spectrum possible, I considered it desirable to perform the most accurate practicable examination of the emanium spectrum, as it had lost the special physical interest to which the above-mentioned interpreta-

tion of it as a gas spectrum pointed. Nevertheless, it remains a noteworthy phenomenon that a solid body, luminous at a low temperature without external addition of energy, should possess a spectrum which shows, not only fairly sharp lines, but also an intensity maximum situated in the ultra-violet. — *Physikalische Zeitschrift*, vi., No. 13, 401.

A MERCURY ARC LAMP WITH QUARTZ VESSEL SUITABLE FOR CHEMICAL PURPOSES.

By FRANZ FISCHER.

THE mercury arc lamp here briefly described is such as I used for my experiments on the effect of ultra-violet light upon glass (*Berichte*, 1905, xxxviii., 946; and *Physikal. Zeit.*, 1905, vi., 216), and also in my research on the formation of ozone by ultra-violet light (*Berichte*, 1905, xxxviii., 2633).



The figure shows the form of this lamp. It consists of an outer glass vessel A, and an inner double-walled vessel B, which is made of quartz, and is exhausted. The quartz cylinder is fixed into the glass vessel by means of sealing wax. Platinum wires are fused in at D and D₁, and from them is suspended the anode X, an iron ring surrounding the quartz cylinder. F represents the connection with the air-pump, and G is a cock with an oblique bore.

At the bottom of the lamp the mercury for the cathode is placed. The lamp is fixed by means of a rubber ring into the neck of an inverted glass flask. Beneath the rubber ring is a tin-foil ring with copper-wire wound round it to enable the lamp to be lighted by means of an inductor. The lower end of the lamp is immersed in a bowl of mercury. Water circulates through the glass flask to cool it.

The aim of the cooling is to lower the temperature in the interior of the lamp, and thus to obtain a lower density of the mercury vapour, which is favourable to the formation of ultra-violet light. The lamp burns with a bluish violet light.

The anode is connected with the positive pole, and the mercury cathode or bowl with the negative. Moreover, the negative pole of the secondary coil of an inductor is

connected with the mercury and the positive pole is connected with the tin-foil ring. As soon as the inductor is set going the direct current passes through the lamp. The strength of the current usually amounts to 5 ampères, and the potential of the lamp to roughly 20 volts.

Although the quartz vessel is double-walled, and the space between the walls is most carefully exhausted, the inner wall always becomes hot rapidly in consequence of the radiation of heat. To obviate this, a specially constructed glass condenser was inserted into the quartz vessel.—Abridged from *Berichte*, 1905, xxxviii., 2630.

SO-CALLED SOLID SOLUTIONS OF INDIFFERENT GASES IN URANIUM OXIDES.

By CARL FRIEDHEIM.

THE important question as to how helium is retained in the uranium minerals has called forth an interesting paper by V. Kohlschütter and K. Vogdt (*Berichte*, 1905, xxxviii., 1419), in which it is shown that it is possible to prepare an artificial uranium compound which, in the opinion of the authors, may be regarded as an "exact model" of the natural compounds containing helium.

This article induced the author to perform the following experiments, and in order to understand them the gist of article must be given here.

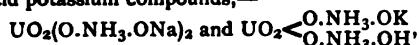
K. A. Kofmann (*Zeit. Anorg. Chem.*, 1897, xv., 75) has prepared a hydroxylamine-ammonia compound of uranic acid, $\text{UO}_4(\text{NH}_4\text{O})_2 + 2\text{NH}_3$, which, when treated with water, gives up ammonia, and yields the substance $\text{UO}_4(\text{NH}_4\text{O})_2 + \text{H}_2\text{O}$, which may be obtained directly from a uranyl salt and excess of aqueous hydroxylamine.

Together with Kohlschütter it was then found (*Zeit. Anorg. Chem.*, 1898, xvi., 463) that the substance possesses an acid character, i.e., the hydroxyl hydrogen of the hydroxylamine residue can be replaced either entirely or partly by ammonium, potassium, or sodium.

Hence the first substance is to be regarded as—



They also succeeded in preparing the neutral sodium and the acid potassium compounds,—



and the correctness of their opinion regarding the nature of the pure hydroxylamine compound was thus supported.*

This canary-yellow coloured compound suffers a change at a high temperature (cf. *Ann. d. Chem.*, 1899, cccvii., 321, et seq.; also *Berichte*, 1905, xxxviii., 1420—1426). If it is strongly heated in a test-tube, it splits, forming black uranium dioxide, ammonia, and water; *in vacuo* considerable heat is developed, and ammonia and nitrous oxide are formed.

But if it is slowly brought to a temperature of 125°, ammonia and water may be shown to be generated, and after heating for two days a fairly constant decrease of weight takes place, amounting on an average to 17.9 per cent, and a dark yellow to blackish brown mass remains behind, which, when heated in a test-tube, no longer pulverises but gives uranium dioxide, large quantities of ammonia, and water.

The product obtained by heating contains on an average 76 per cent of uranium and 4.95 per cent of nitrogen, besides lower oxide of nitrogen (1 mol. UO_2 to 6—8 mols. UO_3), and, when boiled with caustic soda, gives varying quantities of ammonia (maximum, 1.8 per cent), which are regarded as accidental and negligible.

In dilute acids the preparation dissolves instantly, giving rise to an energetic evolution of nitrogen and nitrous

oxide, the volumes of which are approximately in the proportion of 1 to 2, while the original yellow hydroxylamine compound does not behave similarly.

These facts are explained as follows:—On heating the hydroxylamine uranate to 125°, a slow intramolecular transposition of the hydroxylamine occurs, ammonia and water being formed; these two latter escape; moreover, nitrogen and nitrous oxide are also formed, which remain "practically quantitatively" dissolved in "homogeneous mixture" in the uranic acid, which acts only as an "accelerator" of the reaction.

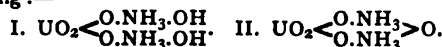
The two gases and the acid "molecularly penetrate" one another, and are examples of "solid solutions of nitrogen and nitrous oxide" in uranic acid; these must decompose with escape of the gases when the solvent is removed, i.e., when the addition of acid converts it into uranyl salt.

Hence the analogy with the behaviour of uraninite and cleveite towards acids, and the authors apparently regard any other explanation of the process occurring on heating the original material and on the decomposition by acids of the product obtained by heating as impossible.

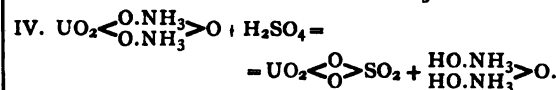
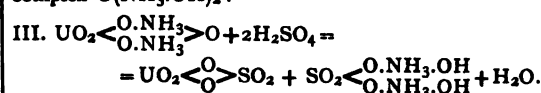
They see also in the product obtained by heating the hydroxylamine uranate a model for the minerals containing helium, although it gives up the "dissolved" gas completely and at a far lower temperature than these on the addition of acids.

It will now be shown that it is possible to explain the process in question in a far simpler manner.

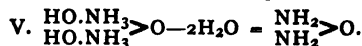
Since, as Hofmann and Kohlschütter (*loc. cit.*) have themselves shown, hydroxylamine uranate (I.) possesses the character of an acid (we may call it hydroxylamine uranic acid), it may by cautious heating be converted into the anhydride (II.), which, mixed with uranic acid,* is present in the dark yellow to blackish brown coloured product of heating:—



This on treatment with acids may not again add on the elements of water† (according to III.), and pass into a mixture of uranyl salt and hydroxylamine salt,‡ but may decompose according to Equation IV. into the first, and a complex $\text{O}(\text{NH}_3.\text{OH})_2$:—



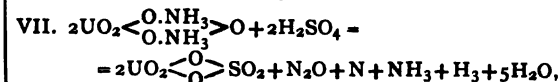
The latter is unstable; first water splits off.



This is the unknown anhydride of hydroxylamine, which is also unstable, and at once decomposes into nitrogen, nitrous oxide, ammonia, hydrogen, and water.



Thus the whole decomposition process of substance II. by means of acids may be represented as follows:—



in which naturally the ammonia cannot escape as such, but remains in solution as primary ammonium sulphate.

* If we assume that 3 mols. of I. give 1 mol. of II. and 2 mols. H_2UO_4 , the loss of weight must amount to 17.25 per cent, while Kohlschütter and Vogdt find an average of 17.90 per cent. Yet according to the experimental conditions less H_2UO_4 may be present than the amount indicated by the amount of U and N.

† Similar cases are known; the difficult change of pyrophosphoric acid and pyrophosphates into the ortho-compounds may be recalled.

‡ Product I. behaves thus.

* Similar substances are derived from many other acids. Cf. the next reference.

Evidently, according to this view, just as Kohlschütter and Vogdt showed, nitrous oxide and nitrogen must escape; but hydrogen must be primarily formed, and its presence was expressly denied by both investigators, and, moreover, ammonia must result, which was certainly found by them, but was regarded as "irrelevant" (see above).

But it may easily be shown that these discrepancies are only apparent, and that Kohlschütter and Vogdt's own researches strikingly confirm the explanation given here.

1. They obtained from their preparation (see above) a maximum of 1.8 per cent ammonia, corresponding to 1.5 per cent nitrogen, and a total of 4.95 per cent N. But for the critical examination of the decomposition process this is not an "irrelevant" amount, but one of considerable importance, which indeed constitutes 0.36 of the total nitrogen, while according to Equation VII. only 0.25 of the total nitrogen appears as ammonia (1 atom from 4 atoms N). Thus the above formula is more than confirmed by this discovery.

2. This excess of ammonia is even an argument in favour of the theory propounded, as evidently one part of the hydrogen first formed combines with the nascent nitrogen to form ammonia.

3. Since it was further expressly stated by Kohlschütter and Vogdt that some uranium trioxide is reduced in the process of solution, the reducing action of the nascent hydrogen evidently manifests itself in this way also, and thus the absence of hydrogen in the gaseous mixture can be explained quite easily.

4. According to the statements of the authors the volumes of the nitrogen and nitrous oxide evolved are approximately in the proportion of 1 to 2. This is also required according to Equation VII.

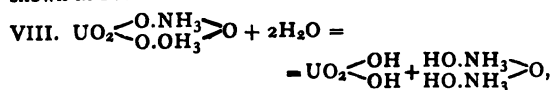
5. As was also stated (*loc. cit.*, p. 1423), hydroxylamine phosphate is decomposed in an exactly similar manner as is here deduced for the uranate, namely (at 130°), into ammonia, nitrous oxide, nitrogen, hydrogen, and a very little oxygen; a further confirmation of the view put forward.

These arguments deduced from Kohlschütter and Vogdt's own results in favour of the theory advanced here may be supplemented by the following:—

1. It was originally the intention of the author to determine whether the product which results on heating hydroxylamine uranate to 125° could be decomposed by water under pressure, so that a larger quantity of the nitrogen present was converted into ammonia. The existence of a solid solution of nitrogen or nitrous oxide in uranic acid would thus be made in the highest degree improbable.

But to my great surprise it was found that the preparation was decomposed by water slowly in the cold, and very quickly at 100°, a fact which has hitherto apparently escaped observation. Gases escape in this case also, but were not further investigated, and ammonia is also formed; when the experiment is suitably arranged this ammonia does not escape, but remains behind as ammonium uranate.

Thus a decomposition process occurs analogous to that shown in IV.



and the uranic acid combines with the ammonia formed according to VI.

This provides an explanation of the otherwise inexplicable fact that on the distillation with caustic soda of the product obtained on heating, which (*cf.* Formula II.) contains no ammonia, the same quantity of nitrogen in the form of ammonia is found as after dissolving it in acids (*cf.* Equations VII. and VIII.), and this behaviour agrees only with the theory here put forward.

(a). 1.8082 grms. of the preparation dried at 120° were heated for several hours with water, with an upright condenser connected with the boiling flask; on account of the

spiriting of the solid residue towards the end, the heating must proceed very cautiously. The crystalline structure is then lost, and the colour becomes more canary-yellow. The exit end of the cooling tube is kept during the whole operation in air-tight connection with a vessel containing 10 c.c. of N/2 H₂SO₄. The contents of this vessel required on titration 50 c.c. N/10 NH₃; thus no trace of ammonia had escaped. The residue in the flask gave on distillation with 33 per cent caustic soda 1.94 per cent NH₃.

(b). 1.7875 grms. of the same preparation were distilled directly with 33 per cent caustic soda. Result, 2 per cent NH₃.

(c). 1.5640 grms. of the same specimen were dissolved in dilute sulphuric acid, and then the distillation with 33 per cent soda was performed, 2.06 per cent NH₃ was found. Both in (b) and (c) 10 c.c. N/2 H₂SO₄ were used, and the ammonia absorbed was determined by titration of the excess of acid with N/10 NH₃.

These results show the correctness of the above statements, and were confirmed when the experiments were repeated. But the results obtained, which always agreed with the same test, as with (a), (b), and (c), varied with different preparations, giving from 1.47 to 1.71 per cent NH₃.

Thus in this case also the amount of ammonia nitrogen varies just as it was proved by Kohlschütter and Vogdt, (*loc. cit.*, p. 1422), and just as, generally speaking, the analytical values* given by them were also found with the author's preparations.

2. The decomposability of the product proved under 1 argues against the assumption of Kohlschütter and Vogdt that a solid solution of nitrogen and nitrous oxide is present in it. For how could the water withdraw the solvent from it? Like sulphuric acid, which dissolves it, *i.e.*, the uranic acid?

The action can be regarded as a chemical action only in the sense of Equation VIII., and as a proof of the existence of the anhydro-compound II.

In conclusion, one more point must be emphasised from the experiments of Kohlschütter and Vogdt. On heating their preparation *in vacuo* they obtain not only the "dissolved" gases nitrogen and nitrous oxide, but also oxygen in quantities, which vary greatly according to the temperature and pressure applied. This behaviour "apparently contradicting," as they say themselves, "the whole assumption of a solution" is most simply explained by the assumption here made that the whole complex, according to the experimental method—on heating rapidly with acids or under lower pressure—can split up in different ways.

We know that the decomposition of the mother-substance, hydroxylamine, may vary essentially, according to the conditions of the experiment, which, moreover, is easily understood if we bear in mind the simultaneous presence of the group NH₂ on the one hand, and also of the group NOH.

The interesting article of Kohlschütter and Vogdt suggests many experiments; it would be very interesting, for instance, to investigate the behaviour of the anhydro-compound when warm towards hydrogen, sulphuretted hydrogen, and towards reduction agents, working in the dry way, on fusing. But I have expressly refrained from this because I wish to avoid any encroachment upon the authors' field of research.

I only wish to show that structuro-chemical considerations, which are in complete agreement with our ideas on valency and with other views, can explain the question at least as satisfactorily as the theory—supported by experimental results—of the "existence of a solid solution of nitrous oxide and nitrogen in uranic acid," and of the "existence of a model corresponding to the minerals containing helium," which is said to result on heating hydroxylamine uranate to 126°.

* The gas analysis experiments were not repeated for the reason given at the end.

I owe hearty thanks to cand. phil. Paul Schulz for his valuable help in preparing specimens and performing analyses.—*Berichte*, 1905, xxxviii., 2352.

A RAPID VOLUMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORIC ACID.*

By W. B. HIRT and F. W. STEEL.

RECOGNISING the necessity for a rapid, and at the same time accurate, method for the determination of phosphoric acid in fertilisers and similar phosphatic materials, particularly in connection with the manufacture of chemical manures, we have lately devoted some considerable time to an examination of various volumetric processes.

The original Pemberton method and its modifications were tried, but discarded in favour of the method described below.

The method described by Dr. Littmann, (*CHEMICAL NEWS*, vol. lxxx., p. 178, or *Chemiker Zeitung*, vol. xx., No. 68), we find, with some alterations, to be one which fulfils the desired conditions, viz., rapid, accurate, easy, and not involving the use of expensive reagents.

The presence of more than very small amounts of bases precipitable by sodium hydrate is detrimental; such precipitates are not always completely dissolved by the sodium citrate, and consequently they obscure the end-points in the titrations.

Practically the only interfering base met with in manures is calcium, and it is most conveniently removed as sulphate; other reagents, such as oxalic acid and ammonium oxalate, were tried for the removal of calcium, but the results proved unsatisfactory. Varying intensity in the light affects the appearance at the end-points of the titrations; strong direct light should be avoided, a moderate steady illumination ensuring regular results.

Organic matter must not be present in sufficient amount to impart a yellow colour to the solution to be titrated. It is best removed by direct ignition; its removal by such means as ignition with magnesium or potassium nitrates is undesirable, as impurities, which may exert a baneful influence upon the work, are thus introduced. Ignition with ammonium nitrate has a tendency to result in mechanical loss. A fact which appears to be common to all volumetric methods for determination of phosphoric acid also obtains in this method, viz., that when comparatively large amounts of phosphoric acid are present in the solution, the results of analysis show greater divergence from those obtained by the gravimetric method than when small amounts of phosphoric acid are present.

Therefore we recommend that when the phosphoric acid in any material exceeds 20 per cent, the weight of the substance used for the determination should be 0.125 gm., while when it is under 20 per cent, 0.25 gm. should be used.

In the former case the c.c.'s. of special soda solution (*vide infra*) required for neutralisation must of course be multiplied by 2 to get the percentage.

The following special reagents are required in addition to the ordinary ones mentioned in the description of the process.

1. Sodium hydrate (approximately normal solution).
2. Sodium hydrate, special. Made by diluting 35.22 c.c. of strictly normal sodium hydrate solution to 1000 c.c. with water. When 0.25 gm. of material is used each c.c. of this solution represents 1 per cent phosphoric anhydride, P_2O_5 .
3. Sulphuric acid solution, corresponding exactly with the special soda solution.
4. Sodium citrate solution 25 per cent (*vide infra*).

5. Acid mixture (A), composed of:—Sulphuric acid conc., 250 c.c.; nitric acid conc., 150 c.c.; and water 100 c.c.

6. Acid mixture (B), composed of:—Sulphuric acid conc., 60 c.c.; nitric acid conc., 100 c.c.; and water 140 c.c.

All reagents must be free from carbonic anhydride, CO_2 .

The sodium citrate solution is prepared as follows:—110 grms. sodium hydrate sticks are placed in a beaker of about 1500 c.c. capacity; 192 grms. of pure crystallised citric acid, $C_6H_8O_7 \cdot H_2O$, are next added, then about 300 c.c. water. A very violent reaction takes place, in consequence of which the temperature rises to $103^\circ C$. when the solution boils, so expelling any carbon dioxide which may be present. Now dilute the solutions slightly and boil for a few minutes to ensure complete expulsion of carbon dioxide.

As the amount of sodium hydrate used is insufficient to neutralise all the citric acid, the solution will now be acid. The beaker is covered and allowed to stand until quite cold, about 2 c.c. phenolphthalein solution added, then with constant stirring, sufficient of a solution of sodium hydrate, free from carbonic anhydride, to produce a faint pink colour; make up to 1032 c.c. (sp. gr. = 1.151) with water, and store in a well stoppered bottle. The addition of about 1 c.c. of ethyl ether to this solution assists in its preservation. The solution is neutralised when required as follows:—The amount likely to be used during the day's work (say 200 to 300 c.c.) is drawn off (filtering through cotton-wool if necessary). 10 c.c. of this is diluted to about 40 c.c. (if the original solution is alkaline, the pink colour of the phenolphthalein appears at once on dilution through ionisation taking place), 0.25 c.c. phenolphthalein added, then standard (N/10) acid or alkali till neutral; from this titration the amount of acid or alkali required for the remainder of the 200 or 300 c.c. of the solution is calculated and added thereto, another 10 c.c. then drawn off and checked for neutrality.

In the above titration vigorous shaking of the flask is necessary.

The acid mixtures are so proportioned that the minimum excess of free acid is left after solution of the phosphate, anything more than a slight excess being very undesirable.

The Working Process.

1. *Phosphoric Anhydride Soluble in Water*.—2 grms. are washed on a filter with water (200 c.c.) in the usual manner. In order to prevent precipitation of calcium phosphate in the solution, about 1 c.c. of sulphuric acid (10 per cent) is added when about 50 c.c. of washings have collected. Any slight precipitate of calcium sulphate may be neglected. Titrate 25 c.c. (= 0.25 gm.) directly, according to directions for total phosphoric acid.

So far as our present experience goes, the amount of soluble organic matter present has been too small to effect this determination in any way.

2. *Phosphoric Anhydride Insoluble in Water and Ammonium Citrate*.—The residue obtained after extraction with water and then ammonium citrate (neutral sp. gr. 1.09) is ignited to a white ash, treated with 5 c.c. of acid B, heated until fumes of sulphuric acid are given off, made up to 100 c.c. with water, and 25 c.c. (= 0.5 gm.) titrated as in (3). Burette reading is divided by 2 to give percentage of phosphoric anhydride.

3. *Total Phosphoric Anhydride*.—2 grms. weighed out. In the absence of organic matter, treat with 5 c.c. acid A at once. Where organic matter is present the 2 grms. of substance are placed in a porcelain dish and heated in the muffle for a few minutes, so that organic matter is carbonised; it is not necessary to incinerate completely, free carbon not being objectionable.

Now transfer the ignited substance to a small beaker, add 5 c.c. acid A, cover the beaker and heat for a few minutes on the sand-bath, remove cover of beaker and continue heating until white fumes of sulphuric acid are

* From the *Proceedings of the Society of Chemical Industry of Victoria*, March—April, 1905.

copiously evolved; cool, dilute with water, again cool and wash into a 200 c.c. gauged flask, using about 150 c.c. water; add from 30 to 40 c.c. absolute alcohol (to throw down as much calcium sulphate as possible), then add water to 200 c.c. mark, mix well, and either allow to clarify by subsidence or filter through a dry filter. Titrate 25 c.c. (≈ 0.25 gm.), *vide infra*. Methylated spirits purified by distillation from sodium hydrate may be used instead of absolute alcohol. After considerable practice the use of alcohol may be omitted, but better results will be got by its use.

The Titration.—This operation requires special care and should be carried out in strict accordance with the following directions.

To the solution obtained as above, add 3 drops methyl orange solution (an excess of methyl orange must be avoided, as it tends to interfere with the end-point in the second titration). Add approximately normal soda solution till nearly neutral (it may be necessary to add 1 or 2 drops more methyl orange), finish off with N/10 soda. Should the end-point be overshoot, titrate back with N/10 sulphuric acid. Now add 10 c.c. sodium citrate solution, and 0.25 c.c. phenolphthalein solution, and titrate with the special soda solution until the usual pink tint appears. The burette reading gives the percentage of phosphoric anhydride directly. N/10 soda may be used in place of the special solution; this is not recommended, however, as there is a very much greater risk of error, the special soda being much more dilute. If N/10 soda be used the factor for 0.25 gm. of substance is 2.84, giving percentage of phosphoric anhydride, P_2O_5 . The factor for 1 gm. is 0.71.

A few results comparing the above method with the gravimetric are appended:—

	Percentages of phosphoric anhydride.	
	Volumetric.	Gravimetric.
1. Superphosphate (non-nitrogenous)	23.61	23.59
2. Superphosphate (nitrogenous) ..	21.65	21.53
3. Bone-dust and superphosphate (mixed)	23.20	23.31
4. Bone-dust	22.12	22.51
5. Bone-meal	25.84	25.92
6. Rock guano	38.81	38.83

Nos. 1 to 5 inclusive. Gravimetric method employed was precipitation as ammonium magnesium phosphate in presence of ammonium citrate.

No 6. Gravimetric method employed was American official molybdate method.

While experiments on the molybdate volumetric methods were in progress, we tried a variety of filters, endeavouring to find one which would enable the yellow precipitate to be conveniently dealt with. The one which we found most satisfactory consists of a layer of pulped filter-paper. It was our intention to deal more fully with this matter of filtration, but in a recent number of the *Journal of the American Chemical Society* (vol. xxvii., p. 287, March, 1905), Shimer describes his work along the same line, simultaneously arriving at the same conclusion as we have, so that we need only refer those interested to the above paper. Shimer finds that the filter constructed according to his directions may be used for a great variety of precipitates. One difference between Shimer's filter and that used by us, is that for some precipitates we find it convenient to use an ordinary funnel into which a perforated disc of aluminium about 15 m.m. diameter, and having a piece of wire of the same metal attached as a handle, is fitted; the felt of paper is laid on about 2 m.m. thick by suction. The precipitate and paper pulp can be very easily washed into the titration flask, by raising the disc slightly by means of the wire handle and directing upon it a jet of water from a wash-bottle.

We desire to express our thanks to Mr. J. Cuming, jun.,

for permitting the publication of the results of our investigations.

Chemical Laboratory, Cuming, Smith, & Co. Pty., Ltd.,
Yarraville, Melbourne, Australia.

Note added July 4, 1905.—Further experiments, with a view to the simplification of the process, are in progress. The following additional comparative figures, between this method and the U.S.A. Official Gravimetric method, show the accuracy obtainable:—

	Percentages total P_2O_5 .	
	A.O.A.C. molybdate.	Volumetric.
Non-nitrogenous superphosphate ..	20.26	20.16
Non-nitrogenous superphosphate ..	20.59	20.73
Nitrogenous superphosphate ..	23.13	23.08
Bone-dust	21.62	21.58

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, June 7th, 1905.

H. A. LENEHAN, F.R.A.S., President, in the Chair.

The following report was presented by Prof. LIVERSIDGE at the Annual General Meeting, May 3rd, 1905:—

International Catalogue of Scientific Literature.

In 1903, I was appointed by the Council of this Society, acting as the Regional Bureau for New South Wales, to represent this State at the Council Meetings held in London in May last. I duly attended the meetings, and now have the honour to make the following report:—The Royal Society of London commenced the work by compiling Catalogues of Scientific Papers (printed between 1800 and 1883) in twelve large quarto volumes, the first volume of which was issued in 1867. In it the titles are arranged solely under the authors' names. A catalogue of the papers published since, *i.e.*, between 1884 and 1900, is now in hand, and a subject index is also nearly completed.

The possibility of preparing a complete catalogue of current scientific literature was considered by the Royal Society in 1893, but as it was apparent that the work was beyond the resources of the Royal Society, or indeed of any single body, the Society sought the opinion of representative foreign bodies and individuals, and the replies being favourable, steps were taken to summon an International Conference. This conference, at which I was present as a Delegate, took place in London on July 14th to 17th, 1896, and was attended by delegates appointed by the Governments of Canada, Cape Colony, Denmark, France, Greece, Hungary, India, Italy, Japan, Mexico, Natal, the Netherlands, New South Wales, New Zealand, Norway, Queensland, Sweden, Switzerland, the United Kingdom, and the United States. It was then unanimously resolved to compile and publish a complete catalogue of current scientific literature, arranged both according to subject matter and authors' names. The Royal Society was requested to appoint a committee to further consider the system of classification to be adopted and other matters, and it was decided to establish a Central Bureau in London.

At the second International Conference held in London on October 11th to 13th, 1898, several questions were settled, and a provisional International Committee appointed which afterwards met in London on August 1st to 5th, 1899, when the work was still further expedited and the Royal Society requested to organise the Central Bureau, and make all necessary arrangements so that the preparation of the catalogue might be commenced in 1901.

A third International Conference was held in London on June 12th and 13th, 1900, at which all financial and other difficulties were removed by the Royal Society agreeing to act as publishers and to advance the funds necessary to start the enterprise. The supreme control over the catalogue is now vested in an International Convention which is to meet in London in 1905, in 1910, and every tenth year afterwards, to re-consider, and if necessary to revise, the regulations for carrying out the work of the catalogue. In the interval between two successive meetings of the Convention the administration of the catalogue is carried out by the International Council, the members of which are appointed by the Regional Bureaus.

The total expenditure from July 1st, 1900, to February 29th, 1904, has been £10,153, and the total amount received from subscribing bodies was £6755; eventually the publication will pay its way, but it may be some time before the debt to the Royal Society will be extinguished. The financial support given by the different countries is shown in the following list. New Zealand has now become a contracting body:—Austria, £165; Canada, £119; Cape Colony, £109; Denmark, £102; Egypt, £17; Finland, £45; France, £754; Germany, £901; Greece, £34; Holland, £133; Hungary, £68; India and Ceylon, £471; Italy, £459; Japan, £255; Mexico, £85; New South Wales, £34; New Zealand, £17; Norway, £85; Nova Scotia, £17; Orange River Colony, £17; Poland, £17; Portugal, £17; Queensland, £34; Russia, £512; South Australia, £34; Sweden, £85; Switzerland, £119; United Kingdom, £765; United States, £1251; Victoria, £17; Western Australia, £17. Total £6755.

It has been suggested that special efforts should be made by the Regional Bureaus to bring the catalogue under the notice of scientific workers, and to secure an increase in the number of subscribers. The whole of the first and second issues of the International Catalogue of Scientific Literature have been published with the exception of the volumes on botany and zoology; the third annual issue is in preparation, and several of them are already in the press. The number of entries in the author-catalogue of the first annual issue was 43,447, and the total number of entries in that issue was 149,768. The numbers of books and papers indexed in the volumes of the second annual issue are as follows:—(A) Mathematics, 1843; (B) Mechanics, 841; (C) Physics, 2433; (D) Chemistry, 5632; (E) Astronomy, 1223; (F) Meteorology, 1988; (G) Mineralogy, 1307; (H) Geology, 1702; (J) Geography, 2022; (K) Palaeontology, 638; (L) General Biology, 689; (M) Botany, 6339; (N) Zoology, 7131; (O) Anatomy, 1424; (P) Anthropology, 1861; (Q) Physiology, 9671; (R) Bacteriology, 3132. The total number of entries in the author-catalogue of the second annual issue is therefore 49,876, an increase of 6429, or about 15 per cent more than the number in the first annual issue. The total number of pages in the first annual issue is 8387.

The accompanying table shows the number of slips received and the instalments in which they were supplied to the Central Bureau.

It was originally intended that the catalogue should not only contain the titles of papers, but that their subject-matter should be fully indexed also; financial considerations have, however, led to the number of subject-entries being at present limited in number. The title slips received at the Central Bureau very often showed that the papers were insufficiently indexed, especially in the lists of new species in botany, zoology, and chemistry; in many cases the Central Bureau has made good these deficiencies. The Executive Committee urge that efforts should be made in all countries to supply fuller information as to the contents of papers; if this were done the catalogue would be much more complete and the cost would be much decreased, and all journals are urged to index each paper and attach the registration numbers at the time of publication.

At the meeting of the International Council held at the Royal Society's House, London, May 23rd and 24th, 1904, it was resolved, in consequence of the success achieved by

Germany	146,552	slips in	59	instalments
France	46,702	"	38	"
United Kingdom . .	43,484	"	166	"
United States . . .	37,688	"	68	"
Russia	21,071	"	5	"
Italy	13,473	"	25	"
Holland	6,657	"	17	"
Austria	6,379	"	2	"
Poland	3,492	"	8	"
India and Ceylon . .	2,231	"	39	"
Japan	2,208	"	10	"
Switzerland	1,932	"	7	"
Hungary	1,745	"	4	"
Denmark	1,722	"	17	"
Sweden	1,457	"	4	"
Victoria	1,445	"	3	"
Norway	1,303	"	12	"
New South Wales . .	1,016	"	5	"
Finland	707	"	8	"
South Africa	645	"	4	"
Belgium	584	"	2	"
Canada	537	"	11	"
New Zealand	327	"	3	"
South Australia . . .	130	"	4	"
Western Australia . .	16	"	1	instalment
	343,503		522	instalments

the International Catalogue of Scientific Literature, and of its great importance to scientific workers, to recommend that its publication be continued. The agreement with the contracting countries was made in the first instance for five years only, in case the publication of the catalogue should fail financially, or in other ways. It was also decided to spend £100 in making the catalogue known, and to take steps to invite the co-operation of other countries not yet represented on the Council, e.g., Spain, the Balkan States, South American Republics, &c.

The proposal to publish additional volumes upon—(a) Medicine and Surgery; (b) Agriculture, Horticulture, and Forestry; (c) Technology (various branches) was discussed, and it was decided that the Executive Committee should take the suggestion into fuller consideration, and bring it under the notice of the International Convention in July, 1905. It was also resolved that all alterations in the schedules should be collected and edited by the Central Bureau prior to submission to the Regional Bureaus for their opinions, and that the schemes should be edited by a special committee before being submitted to the International Convention.

(Signed) A. LIVERSIDGE.

The following paper was read:—

"On the so-called Gold-coated Teeth in Sheep." By A. LIVERSIDGE, LL.D., F.R.S., Professor of Chemistry, University of Sydney.

Paragraphs have appeared recently in some of the London and Sydney newspapers, stating that gold-coated teeth have been found in Australian sheep. I have recently received the lower half of a sheep's jaw-bone from Dubbo, the teeth of which are more or less completely incrustated with a yellow metallic substance, but more like iron pyrites (marcasite) or brass than gold. The deposit is about $\frac{1}{8}$ of an inch, or less than 1 m.m. in thickness. Under a half inch objective it is seen to be made up of thin translucent layers, but there is no recognisable organic structure. The metallic lustre is due to the way in which the light is reflected from the surface of the superimposed films. The scale partly dissolves in dilute acids. The residue consists of filmy organic matter, still possessing a metallic sheen although white in colour instead of yellow. The chemical examination shows that the incrustation on the teeth is merely a tartar-like deposit made up principally of calcium phosphate and organic matter.

Note.—Prof. Liversidge also showed a calculus of a similar metallic-looking character from a sheep's stomach,

deposited in distinct layers round a piece of twig, but of rather a darker bronze tint than the substance on the teeth. This specimen belongs to the Sydney Technological Museum, and was kindly lent for exhibition by the Curator, Mr. R. T. Baker.

NOTICES OF BOOKS

Atlas of Emission Spectra of most of the Elements. By AUGUST HAGENBACH, Ph.D., and HEINRICH KONEN, Ph.D. Authorised English Edition by ARTHUR S. KING, Ph.D. Jena: Gustav Fischer. London: William Wesley and Son. 1905.

THIS atlas contains heliographic reproductions of photographs of the spectra of all the elements with a very few exceptions, taken by the authors with a small Rowland grating. Twenty-eight charts are given, showing all lines separated which have an interval of $0.8 \text{ A.U.} = 0.08 \mu$, and though naturally the charts cannot reproduce the full detail of the actual photographs, the technical difficulties occurring in their preparation have been most successfully surmounted, and the work will be found of great value in the laboratory. Only the strongest lines outside the sensitive region are given, owing to the impossibility of obtaining both the actinic part and the limiting region on the same plate. The charts are accompanied by descriptive notes pointing out the material used, and the impurities present, and emphasising those features which are actually to be seen in the charts, either with the naked eye or with a lens; a chapter of useful spectrographic notes is also added. The translation has been made from the proof-sheets of the German edition, and every effort has been made to ensure the accuracy of the wave-lengths, which have been checked as far as possible by the original tables.

Analyse Chimique Minérale. Choix de Méthodes. ("Inorganic Analysis. Selected Methods"). By EUG. PROST. Paris and Liège: Ch. Béranger. 1905.

THE aim of this book is to collect all that is indispensable for the analytical chemist, to enable him to cope with the analysis of samples of the most common substances met with in practice. Under the headings of the individual metals and acid radicals, the characteristic reactions, methods of qualitatively demonstrating the presence, and a selection of methods of determination and separation of the ions are given. The introduction contains a short description of elementary processes and operations, which seems to suggest that the author had in view the needs of beginners, for whose use, however, we should not recommend the book. No attempt is made to provide a course of graduated difficulty, and in many cases the directions are not sufficiently explicit for students. Moreover, in a book for beginners, hints are required to show how time may be economised to the utmost, and also special pitfalls and sources of error should be pointed out. For the benefit of the analyst some elementary matter might have been replaced by a greater choice of methods; for instance, in a case of such importance as the separation of chlorides, bromides, and iodides it would have been better to give a description of additional processes.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 6, August 7, 1905.

Calcium Chloroborates.—L. Ouvrard.—The natural mineral boracite can be artificially manufactured. Analogous compounds can also be formed in which the magnesium is replaced by iron, zinc, cadmium, &c., and the chlorine by bromine or iodine. The author describes in this paper the products which he prepares by the substitu-

tion of calcium for the magnesium, and of which the preparation presents a certain interest. He separates the chloroborate, $5\text{B}_2\text{O}_3 \cdot 3\text{CaO} \cdot \text{CaCl}_2$, in the form of prismatic crystals, which are insoluble in water and dilute acetic acid, but easily decomposed by the stronger acids, even when very dilute. He also prepares the compound $3\text{B}_2\text{O}_3 \cdot 3\text{CaO} \cdot \text{CaCl}_2$, which presents a totally different appearance.

Constitution of Disymmetric Diparaditolylethane, Dihydride of 2.7.9.10-Tetramethylanthracene, and 2.7-Dimethylanthracene.—James Lavaux.—The author establishes the fact that, if he uses the same constants as those used by Anschütz in his experiments (*Liebig's Annalen*, ccxxxv., p. 313) on tetramethyl anthracene hydride containing the groups CH_3 in 2.7.9.10, his own carbide B, which is prepared by removing the methyls 9 and 10, is the 2.7-dimethylanthracene.

Absorption Spectrum of Manganese Salts.—P. Lambert.—To determine the absorption spectrum of any substance, it has to be purified as far as possible from foreign bodies. To this end, the author purified a solution of manganese dioxide in nitric acid by a large number of precipitations, according to Beilstein's method. The pure dioxide thus prepared is dissolved in hydrochloric acid free from iron. This chloride gives a very characteristic absorption spectrum, consisting of bands between the following wave-lengths:—

I.	Between λ 557.50 and λ 513.00
II.	" 442.50 " 420.00
III.	a. " 412.25 " 410.25
	b. " 408.00 " 405.25
	c. " 403.25 " 402.06
	d. " 401.00 " 400.00
	e. " 397.75 " 396.25
	f. " 395.75 " 394.50

The author does not believe that manganese alone presents this spectrum, but he intends to further investigate the matter.

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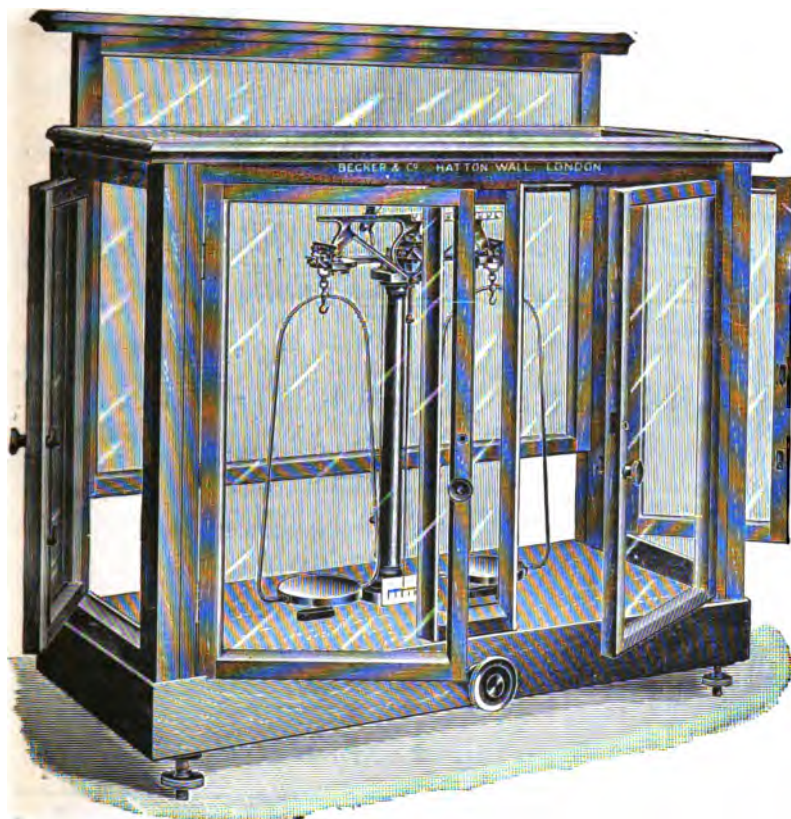
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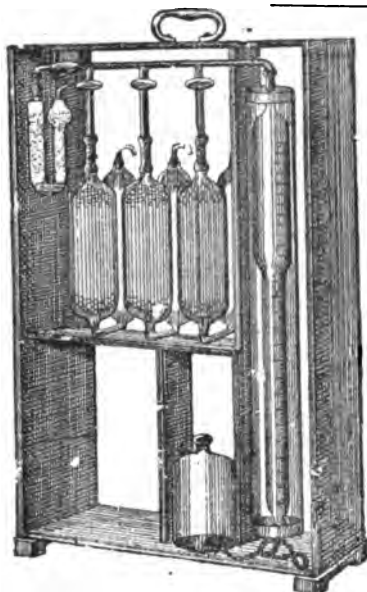
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THE CHEMICAL NEWS.

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(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following five subjects:—(1) English; one paper of three hours. (2) Elementary Mathematics; two papers of three hours each. (3) Latin or Elementary Mechanics, or Elementary Physics—Heat, Light, and Sound, or Elementary Chemistry, or Elementary Botany; one paper of three hours in each subject. (4) and (5) Two of the following subjects, neither of which has already been taken under Section (3); one paper of three hours in each subject; if Latin be not taken, one of the other subjects selected must be another Language from the List, either ancient or modern:—Latin, Greek, French, German, *Arabic, *Sanskrit, *Spanish, *Portuguese, *Italian, *Hebrew, Ancient History, Modern History, Logic, Physical and General Geography, Geometrical and Mechanical Drawing, Mathematics (more advanced), Elementary Mechanics, Elementary Chemistry, Elementary Physics—Heat, Light, and Sound, Elementary Physics—Electricity and Magnetism, Elementary Biology—Botany, *Elementary Biology—Zoology. Candidates in subjects marked with asterisk must give at least two months' notice before the commencement of the Examination.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Several valuable Scholarships and Exhibitions are available to students.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously. In the years 1905 and 1906 only, candidates will be enabled to pass this Examination without the prescribed knowledge of French and German.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.

Lees Reader in Chemistry—G. Brereton Baker, M.A.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Emmanuel, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN. TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramaden, F.C.S.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.

2. *Organic Chemistry*.—General, second year; advanced, third year.

3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. These Foundation Scholars receive £20 per annum, have free commons, their chambers for half the charge paid by other students, and their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(DIVISION OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.

Assistant Professor—Herbert Jackson, F.C.S.

Lecturer and Demonstrators—P. H. Kirkaldy, F.C.S., D. Northall Laurie, F.C.S., S. W. Collins, and L. Hinkel.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1905-1906 are Oct. 4, Jan. 9, and April 30.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *visd voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry: Winter Session, £5 5s.; Summer Session, £3 3s.; Course, £8 8s. Practical Chemistry: Winter Session, £5 8s.; Summer Session, £4 4s. Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, A.R.S.M., F.I.C., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

For particulars apply to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professors—Sir William Ramsay, K.C.B., LL.D., F.R.S. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—E. C. C. Baly, F.I.C.; J. K. H. Inglis, B.Sc., M.A.; N. T. M. Wilmore, M.Sc.; and S. Smiles, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 3 to December 20; Second Term, from January 9 to March 30; Third Term, from May 1 to June 16. Class Examinations begin June 18.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Friday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

Fees:—For the Course, £7 7s.; for the First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Senior Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning in January.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent Chemical Theory researches.

Third Term: Some Lectures will also be given on Saturdays at 9, during the Third Term, on the History of Chemistry.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

Organic Chemistry.

Mon., Wed., and Fri., at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the preceding Course, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d. for a Second Course, £3 3s.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratories are open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

ROYAL COLLEGE OF SCIENCE AND
ROYAL SCHOOL OF MINES.

Professor of Chemistry—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—M. O. Forster, Ph.D., D.Sc.

Demonstrators—H. Chapman Jones; G. T. Morgan, D.Sc., A.R.C.S.; and J. C. Philip, M.A., Ph.D., B.Sc.

Assistants—G. S. Newth and Miss Whiteley, D.Sc., A.R.C.S.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Board of Education. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction lasts for three years, is the same for all the divisions during the first year, after which it is specialised according to the particular division in which the student is working for the Associateship.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject except Mining and Metallurgy and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	£	£
Physics	3	13
Biology with Botany	5	12
Geology with Mineralogy	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	

The fee for the course of Mine Surveying is £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

The Session is divided into two Terms. The first Term begins about the first week of October, and ends about the middle of February. The second Term begins in the middle of February, and ends about the middle of June.

The hours of study are from 10 a.m. to 1.15, and from

2 to 4 or 5 p.m. every day, except on Wednesday and Saturday, when the College closes at 1 p.m.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-fourth Session will commence on Oct. 2, 1905. *Professors*—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C. (Dean); Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. UNIVERSITY OF WALES.

Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Assistant Lecturers and Demonstrators—A. Brooke, Ph.D. (Strass.), and T. C. James, B.A. (Cantab.), B.Sc.

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

Lecturer on Dyeing—(Vacant).

The College is open to male and female students above the age of sixteen years. The Session commences on Oct. 3rd, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1905-1906, Course A). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturer and Demonstrator, Alice E. Smith, B.Sc. Assistant Lecturer in Agricultural Chemistry, Alan Baguley, B.Sc., F.I.C. Junior Demonstrator, Edward Jones, B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 3rd, 1905. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Inorganic and Physical Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Ferman, D.Sc., F.C.S.

Demonstrator—R. D. Abell, D.Sc.

The Session commences October 3rd, and terminates on June 29th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science of the University of London. Fee, £4 4s.

The Senior Course consists of about 50 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Morris W. Travers, D.Sc., F.R.S.

Assistant Professor—Francis E. Francis, D.Sc., Ph.D.

Lecturer—Oliver C. M. Davis, B.Sc., A.I.C.

Lecture Assistant—J. H. Sturgess.

The session 1905-1906 will begin on October 3. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical

and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Elementary Course.—Three Lectures a week will be given during the Session. Fee, £3 13s. 6d.

Special Course.—A special course of Lectures is also given to Elementary Teachers.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Advanced Course.—Two Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Organic Chemistry.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d. An advanced course of lectures will also be given one day a week during the session. Fee, £2 2s.

Practical Chemistry.—Laboratory Instruction.

The Chemical and Metallurgical Laboratories will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

Days per Week ..	Five.	Four.	Three.	Two.	One.
Per Session	15	12½	10	7½	5
" Two Terms ..	11	9	7½	5½	3½
" One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

EVENING LECTURES.

A course of Lectures, which is subject to variation to suit the requirements of Students, will be delivered during the First and Second Terms. Fee 7s. 6d.

Pharmaceutics.—During the first and second Terms a course of Lectures will be given one evening a week dealing chiefly with the *Materia Medica*, Pharmacy, and Chemistry of the British Pharmacopœia. Fee, £1 1s.

Practical Chemistry.—Laboratory Instruction.—The Laboratory will be open one evening a week from 6 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—Two Terms, 21s; One Term, 12s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar.

**MERCHANT VENTURERS' TECHNICAL
COLLEGE, BRISTOL.****CHEMISTRY AND METALLURGY.***Professor*—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.*Lecturers*—G. P. Darnell-Smith, B.Sc., F.I.C., F.C.S.;
H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc.*Demonstrators*—E. H. T. Parker; P. W. Alloway;
C. D. Fuller.*Assistants in Chemical Laboratory*—H. E. Phipps and
J. H. Leonard.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (or forty Students working at one time), Senior Laboratory, Balance Room, Combustion Room, Store Rooms, Metallurgical Laboratory, and Research Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Principal; and the Courses provide completely for the Prel. Sci. Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. and D.Sc. degrees of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Day Classes re-open on Sept. 19, and the Evening Classes commence on Monday, October 2.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (free).

UNIVERSITY OF BIRMINGHAM.*Professor*—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S.*Assistant Lecturers and Demonstrators*—Alex. McKenzie, M.A., D.Sc., Ph.D.; Alex. Findlay, M.A., D.Sc., Ph.D.; T. S. Moore, B.A.; C. K. Tinkler, B.Sc.

The Session will be opened on October 2nd, 1905.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. Mondays to Thursdays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—*Advanced Organic Chemistry.*—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General and Physical Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms ..	13	8½	7½	5
Three Terms ..	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.**DEPARTMENT OF CHEMISTRY AND DYEING.***Head of Department*—Prof. W. M. Gardner.*Lecturers in Chemistry*—B. North, A.R.C.Sc. (Lond.)
L. L. Lloyd, Ph.D.; S. F. Stell, F.C.S.*Demonstrators in Chemistry*—S. R. Illingworth and
N. E. Scafe.*Lecturer in Physics*—J. A. Tomkins, A.R.C.Sc. (Lond.).*Demonstrator in Physics*—E. B. Walker.*Lecturer in Dyeing*—A. B. Knaggs, F.C.S.*Demonstrator in Dyeing*—L. Minikin.*Lecturer in Gas Manufacture*—W. Cranfield.*Lecturer on Botany, Biology, and Pharmacy*—W. West,
F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over four years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Extending over one or two years.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.)*, London.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

IX. Attendance at the College Courses and College Certificates in Chemistry, Physics, Animal Biology, and Botany are recognised by the Conjoint Board for Medical Studies.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc.

Lecturer on Physical Chemistry—H. M. Dawson, B.Sc., Ph.D.

Assistant Lecturers and Demonstrators—C. E. Whiteley, M.Sc., and W. Lawson, B.Sc., F.I.C.

Demonstrator—W. H. Perkins, B.Sc.

The Session begins October 4, 1905.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon. Fee £3 13s. 6d.

5. Honours Courses.—(a) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £2 12s. 6d. (b) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £1 11s. 6d. (c) Physical Chemistry: Tuesday, Thursday, and Saturday at 9.30 a.m. in the Second and Third Terms; fee, £2 12s. 6d. (d) Electro-chemistry: One hour weekly; 31s. 6d.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from January to March. Fee, £5 5s.

Elementary Science for Teachers.—Saturdays, 9.30 to 12.30, for half the session. £2 12s. 6d.

Dyeing and Tinctorial Chemistry Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Assistant—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—A. B. Steven, B.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Lecturer and Demonstrator—F. Kopecky.

Demonstrator—Harold Brumwell.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, viz., the Salt, Akroyd, Brown, Baines, Emsley, Craven, Wheatley, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Chemistry—J. Campbell Brown, D.Sc.

Professor of Physical Chemistry—F. G. Donnan, M.A., Ph.D.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Demonstrators and Assistant Lecturers—A. T. de Moulpied, M.Sc., Ph.D.; F. J. Brislee, M.Sc.; A. Rule, M.Sc., Ph.D.; and E. Garratt, M.Sc.
Assistant—H. H. Froyell.

The Session commences October 1st.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Classes. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Metals and Non-metals. Fee, £3.

Course C.—Inorganic Chemistry. Fee, £3.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Special Organic Subjects. Fee, £2.

Course F.—Physical Chemistry. Fee, £2.

Course G.—Advanced Physical Chemistry. Fee, £2.

Course H.—History of Chemistry and Chemical Philosophy. Three Terms. Fee, £2.

Courses I.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Applied Electro-chemistry. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Examination of Water and Air, &c.

Chemical Laboratory.

The Chemical Laboratories recently enlarged provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water Analysis, Gas Analysis, Photometry and Photography, Electro-chemical Work, Metallurgy Laboratories, a Research Laboratory, and a Museum. New stores for students' apparatus and chemicals have also been provided and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

D.P.H. Course (see special syllabus).

Course for Dental Degree (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German.

First Year.—Chemistry—Courses B and D; Chemical Laboratory three days per week; Technological Chemistry, Course J. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, part of First Year Course. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Courses C and F, Technological Chemistry, Course J. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the B.Sc. Degree of the University of Liverpool, or the later Exam. of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are the possible alternatives:—1. Courses G, H, and J. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses F, H, and J. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses F and I, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week.

Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1906, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15, 1906. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

The Prospectus containing particulars may be obtained from the Secretary, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturer and Demonstrator—J. A. Smythe, M.Sc., Ph.D.

Demonstrator—A. A. Hall, M.Sc., Ph.D.

First Year Courses.—1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on

Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 4th. Fee, £3 10s. for the Session.

11. Special Course.—More advanced than the above. Wednesdays and Fridays, 11 to 12. Fee, £3 10s. for Session.

For Diploma in Electrical Engineering.—Tuesday, 12 to 1. A course of Lectures will be given dealing with the Principles of Chemistry, Fuel, the Phenomena of Combustion, and Metals and Alloys employed in Engineering, &c. Fee for the course, £2.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 3rd. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, H. Dean, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. **Laboratory Fees.**—Student working two days, £3 10s. per term, £9 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in the following subjects:—Arithmetic; English Essay; Geometry; the subject-matter of Euclid, Books I., II., III.; Algebra, up to and including Quadratic Equations. Also any two of the following:—English Language; Latin, including Grammar and Easy Sentences; Greek; French; German; Geography. The next examination commences on September 25. Names to be sent in at least ten days before this date. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—1. The first examination for the Degree of B.Litt. 2. Durham Examination for certificate of proficiency in General Education, held in March and September. 3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end

of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining, and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in September next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 25th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction. Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 25th. Candidates should send in their names to the Secretary on or before September 19th.

THE UNIVERSITY OF MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., M.Sc., F.R.S.

Professor of Organic Chemistry.—W. H. Perkin, Ph.D., F.R.S.

Lecturers and Demonstrators.—G. H. Bailey, D.Sc., Ph.D.; D. L. Chapman, B.A.; Norman Smith, M.Sc.

Assistant Lecturers and Demonstrators.—D. Trevor Jones, M.Sc.; C. H. Burgess, M.Sc.; E. C. Edgar, B.Sc.; C. Weizmann, Ph.D.

Lecturer in Organic Chemistry.—J. F. Thorpe, Ph.D.

Lecturer in Metallurgy and Fuel.—W. A. Bone, D.Sc., Ph.D., F.R.S.

Lecturer in Electro-Chemistry.—R. S. Hutton, D.Sc.

The Session begins on October 4, 1905.

The Chemical Classes form part of the Courses for Degrees in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during the Lent Term.

These courses are intended for Medical Students and others commencing the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Short Courses in Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Thursdays, at 9.30, during the two Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: Two hours per week during the Michaelmas Term.

Applied Electro-chemistry.—One hour per week during Lent and Easter Terms. A course of six lectures on the Electric Furnace and its Applications will be given on Saturday afternoons during the Michaelmas Term.

Applied Chemistry.—(1). Sulphuric Acid and Alkali Manufactures; General Principles of Chemical Engineering. (2). The Natural and Artificial Colouring Matters and the Principles of Dyeing and Printing. (3). The Chemistry of Fuel; the Manufacture of Illuminating Gas and Gaseous Fuel.

Chemistry Laboratory Courses.

During the first year, the student works in the "Roscoe" or the "Dalton" Laboratory at Qualitative Analysis and Inorganic Preparations. Second Year Students work at Quantitative Analysis, and also take a Laboratory Course in Physics or some other subject. Third Year Students work in the "Schorlemmer" Laboratory of Organic Chemistry, and may also undertake experimental work in some special branch of Chemistry.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Metallurgical Laboratory.—This has been recently much enlarged and re-equipped, mainly with a view to post-graduate work on the Structure of Metals and the Chemistry of Fuel.

Applied Organic Chemistry.—In connection with the "Schorlemmer" and "Schunck" Laboratories, a special laboratory is fitted with apparatus and appliances suitable for investigations on Dyes and other organic substances on a large scale.

Electro-chemical Laboratory.—In addition to such apparatus as is required for experimental work on Electrolysis and the Electro-deposition of Metals, special equipment is provided for investigations with the Electric Furnace.

Chemical Research.

In addition to the facilities mentioned above for Metallurgical and Electro-chemical Research, the following laboratories are available for post-graduate work:—(1) The private Laboratories of the two Professors; (2) The "Frankland" Laboratories for Physical Chemistry; (3) The "Schunck" Laboratory for Organic Chemistry; (4) The "Thorpe" Laboratory for Organic Chemistry.

To encourage post-graduate work of this kind, the University gives a "Beyer" Fellowship (£100 per annum) and Scholarships (£25 or £50 per annum).

The "Dalton" Chemical Scholarship (£50 per annum, tenable for two years) is also awarded, and the 1851 Exhibition Scholarships (£150) may be held in the Laboratory. Further, Honorary Research Fellowships and Research Studentships are granted from time to time to those who are capable of carrying out original investigations.

Two "Schunck" Research Assistants are appointed annually, and it is proposed to establish a "Schunck" Fellowship.

Courses for Degrees.

To qualify for the Ordinary Degree of B.Sc. Students have to attend a prescribed course of study extending over three years, and are recommended to pass the Matriculation Examination before entrance. (Subsequent to October, 1906, three years attendance after matriculation will be compulsory).

The course of the Degree of B.Sc. with Honours in Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); an additional course (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Physical or some other Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Lecture course in some Special Branch of Chemistry; History of Chemistry; Chemical Laboratory (5 days per week, for one of which attendance in another Laboratory may be substituted).

For the M.Sc. Degree post-graduate work is required. The D.Sc. may be obtained after four years from graduation, provided that the candidate has distinguished himself in research.

Certificate in Applied Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. Sand, Ph.D., M.Sc.; and R. E. Rose, Ph.D.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 2nd, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—A. N. Meldrum, D.Sc.; W. E. S. Turner, M.Sc., B.Sc.; W. J. Jarrard, B.Sc.

The Session will commence on October 4th.

Matriculation Course.—Tue-day and Friday at 9.30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Intermediate Course for B.Sc. or M.B.—Monday, Tuesday, Thursday, and Friday, at 9.30 a.m.; £3 13s. 6d., and nine hours per week Laboratory work.

B.Sc. Course.—Monday, Tuesday, and Friday, and another hour to be arranged, £5 15s. 6d., and twelve hours per week Laboratory work during two Sessions.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board of Education, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lecture Class and Laboratory, on Wednesday evening. Sessional Fee, £1 10s. Fee for one term, 17s. 6d.

DEPARTMENT OF METALLURGY.

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students engaged in Collieries or Gas-Works.

A new steel works has recently been erected in connection with the Sheffield College at a cost of about £10,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works is also provided with a hammer capable of dealing with four-inch ingots. Differential annealing furnaces, oil brightening and lead-tempering tanks will constitute part

of the new plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumaden, Ph.D., D.Sc., and J. K. Wood, D.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 16th, and ends on March 21st. The Summer Session extends from the middle of April to the end of June.

The Junior Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—Francis W. Gray, M.A., B.Sc., and John Alexander, M.A.

I. General Lecture Course (100 Lectures).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. Special Lecture Course on Organic Chemistry (50 Lectures).—Daily during the Summer Session. Fee, £3 3s.

III. Practical Course for Medical Students.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £4 4s.

IV. Chemical Laboratory.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £4 4s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

V. Physical and Advanced Inorganic Chemistry (30 Lectures).—In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Mr. F. W. Gray. Fee, £2 2s.

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., A.I.C., and W. J. Profeit, M.A., B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to

take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. Agricultural Chemistry (General Course).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. Laboratory.—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. An Intermediate Course of Organic and Advanced Inorganic Chemistry is held in summer; fee, £2 2s. There is also a class on History of Chemistry or Chemical Theory, by Dr. Dobbin; fee £1 1s.; and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis), Physico-chemical Measurements, Agricultural Chemistry, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (i.e., Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—Bertram D. Steele, D.Sc.; Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; and Dr. Emil Westergaard.

The Session begins October 3th, 1905.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Chemistry Students in the fourth year arrangements have been made for their spending twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory has been provided for the study of Micro-

organisms in connection with Brewing, Distilling, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Butter and Cheese Manufacture.

Matriculation Fee, 5s.; Composition Fee for Engineering Courses, £12 12s. per Session; for Chemistry Courses, First Session, £12 12s.; Second Session, £12 12s.; Third Session, £15 15s.; Fourth Session, £15 15s. Full particulars are published in the Calendar of the College early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 26. Entrance Examination Sept. 18.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1905-1906 may be had from Mr. H. F. Stockdale, Secretary; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 13th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for forty Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 29th and following days. Twenty-five of these Bursaries are restricted to Men, one to Men or Women, and fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only

cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s., and for the Advanced Course £5 5s.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—Chemistry.—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—Practical Chemistry.—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—Laboratory Pupils.—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—John Hawthorne, Ph.D., F.C.S.

The College Session will commence on October 17th,

1905, and end on June 9th, 1906. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be specially arranged as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1906.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics, First-class value £42, and Second-class value £21, together with other prizes, e.g., a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C., F.C.S.

Demonstrator—Miss Rosalind Clarke, B.A.

Research Assistants—W. Sloan Mills, M.A., and Percy C. Austin, M.A.

The College Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Prepara-

tions, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by four Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Dean of Faculty and Professor of Chemistry—W. N. Hartley, F.R.S., D.Sc.

Lecturer on Organic Chemistry—Alphonsus O'Farrelly, M.A.

Senior Assistant—J. Holms Pollok, D.Sc.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships include free education for the full Associateship Course of three years and maintenance allowance of a guinea a week during the Session.

**CHEMICAL LECTURES, CLASSES, AND
LABORATORY INSTRUCTION.**

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme

of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 19th, and the Winter Session opens on Tuesday, October 3rd. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 19th. Session begins October 3rd. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School, commences Sept. 18. Session commences October 2.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh.Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vit.), assisted by Mr. John L. White, D.Sc., Mr. H. Evans, and others. Session opens Sept. 25. Complete courses of instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Paper Testing, Paper Making, Gas Analysis, Oils, Fats, and Soaps, Chemistry of Building Materials, Chemistry of Foods, &c.

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. J. E. Mackenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. This Institution, which has now completed eighty-two years of educational work, will commence the new Session on Monday, October 2, when the Right Hon. Sir Edward Fry will give the Opening Address, at 7.30 p.m. The

Day and Evening courses of study comprise the various branches of Natural Science (Chemistry, Physics, Botany, Zoology, Geology, &c.), Mathematics, Latin, Greek, Modern Languages, Economics, Law, Logic, and Commercial Subjects. Courses conducted by recognised teachers of the University provide for the Examinations of the University of London, in the faculties of Arts, Science, Commerce, and Law. The Report for the last session shows that during the year 84 students passed some University examinations, while a large number gained successes at various public examinations. The College has added considerably to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are very thoroughly equipped. Courses in Mining, Metallurgy, and Assaying are given both in the day and evening. The Modern Language classes include Italian, Spanish, and Russian, as well as French and German. The College has a School of Art, open both day and evening. Good Reading and Magazine Rooms are provided. The Calendar supplies detailed information respecting the Courses of Study, Examinations, Studentships, &c. A popular Lecture or Entertainment is given in the Theatre every Wednesday evening from October to May.

BRIXTON SCHOOL OF CHEMISTRY AND PHARMACY, 171, Brixton Road, London.—Principal, Dr. A. B. Griffiths, F.R.S.(Ed.). Lectures on Inorganic and Organic Chemistry, Physics, Botany, &c., for Pharmaceutical, Medical, and other students. The benches in the laboratory are fitted with every convenience. There are courses in Research Work. Full particulars as to fees, &c., may be obtained by writing to the Principal.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road, S.E.—Chemistry: Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry (Session fees, per course, 10s. to 20s.). Day Practical class in Electro-chemistry, lecture on Friday evenings. Special Saturday Morning Class in Practical Chemistry (10s.); Dr. F. Mollwo Perkin, assisted by H. B. Law, B.Sc. Electricity and Magnetism: Evening Lectures and Laboratory Work (Session fees, per course, 10s.), Dr. J. Henderson, assisted by H. Saunders. Special Evening Courses on Painter's Oils, Colours, and Varnishes. Special Day Courses in Technical Chemistry and Electro-chemistry (October to July), £10. Session opens Monday, Sept. 25.

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Intermediate Science, and B.Sc. Examinations of the University of London. The Day Course in Chemistry is of three years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, 1d., by post 3d.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Lectures and Practical Classes in General Chemistry and Photography, also in Chemistry applied to other industries, are held in the evenings from 7.15 to 10, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties. Session commences September 21.

EAST LONDON COLLEGE, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., Ph.D.; Assistants, Clarence Smith, D.Sc., and F. G. Pope. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to work for the

Honours Examination and research. Evening Classes for London University Degrees are also held. The Day College opens on Sept. 18. Evening Classes begin Sept. 25.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

IMPERIAL COLLEGE OF CHEMISTRY AND PHARMACY, 49 and 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *vs* the Institute of Chemistry Examination. Students attending the College visit technical work.

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Principal, Charles A. Keane, M.Sc., Ph.D., &c., assisted by R. S. Willows, D.Sc., and C. O. Bannister, A.R.S.M. Evening Classes in Chemistry, Metallurgy, Physics, and Mathematics, designed to meet the requirements of those engaged in Chemical, Metallurgical, and Electrical industries, and also in other departments of Science and Art. Practical laboratory work. Courses of Instruction in Glass Blowing, by A. C. Cossor. Classes begin September 25. Full details may be obtained on application, or by letter to the Principal.

THE POLYTECHNIC, 309, Regent Street, W.—University of London Preparation Classes.

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, (i.) to promote the better education of persons desirous of becoming public and technical analysts and chemical advisers on scientific subjects; (ii.) to examine Candidates, and to grant certificates of competency; and (iii.) to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship*.—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University approved by the Council, or in the laboratory of a Fellow of the Institute, with the object of adopting the profession of Analytical and Consulting Chemistry. *The Intermediate Examination*.—Candidates for admission to the Intermediate Examination are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Advanced Mathematics; (ii.) Mechanics and Chemical Engineering; (iii.) Metallurgy; (iv.) Geology and Mineralogy; (v.) Physiology; (vi.) Bacteriology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' training in a recognised Institution as indicated above, and work systematically for two other years in the laboratory of a Fellow of the Institute. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also passed in at either the Final or Intermediate University Examination)

in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship (A.I.C.)*.—Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship (F.I.C.)*.—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of Applied Chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained on application to Messrs. Bladell, Taylor, and Co., 173, Upper Thames Street, London, E.C. Price One Shilling.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Mr. Robert H. Pickard, D.Sc.(Lond.), &c., assisted by Messrs. Jos. Yates, W. O. Littlebury, and H. L. Leach. Session opens Monday, September 11. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 2d.).

COUNTY TECHNICAL LABORATORIES, Chelmsford.—The new buildings are now open, and comprise facilities for practical instruction in Chemistry and Biology in their relation to Agriculture. Lecturer in Agricultural Chemistry, T. S. Dymond, F.I.C.; Assistants, G. Clarke, A.I.C., and others. Prospectus free on application.

REDRUTH SCHOOL OF MINES, CORNWALL.—Principal, Howard C. Ridding, A.R.S.M., F.I.C., assisted by a staff of Mining Engineers and Mine Surveyors. Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, &c., for intending Assayers, Mineral Chemists, and Surveyors. Shorter Courses are also held in the above-named and cognate subjects to meet the requirements of intending Mining Engineers and Prospectors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application to the Registrar. Session commenced Wednesday, Sept. 13.

LEEDS INSTITUTE: TECHNICAL SCHOOL, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc.(Lond.), A.R.C.S. Evening Classes are held in over sixty subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by Mr. R. E. Barnett, B.Sc., A.R.C.S.; Mr. J. B. Murray, Mr. A. McFarlane, and Mr. F. R. Penn; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Magnetism and Electricity, Practical Physics, Electro-plating, &c., by Mr. J. E. Tindall, B.A., B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker; Photography, by Mr. S. E. Bottomley. Fees: 5s. to 10s. 6d. per class per session. Group courses arranged for Pharmaceutical Students and for those engaged in Chemical Industries at composition fees. Session commences Sept. 18th. Prospectuses of various Classes free on application to the Secretary, Mr. Arthur Tait. Calendar of the Institute (242 pp.), post free 5d.

THE MUNICIPAL SCHOOL OF TECHNOLOGY, Sackville Street, Manchester.—This fine building occupies an area of upwards of 6800 square yards, and is six floors in height. Its equipment, which is nearly complete, is on a scale of great magnitude. It comprises laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, for the Textile industries, for Photography, Collotype and Photo mechanical processes, for the Letterpress and Lithographic industries, and for the industries included within the scope of Architecture. The provision for

the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises, in addition to ample accommodation for pure Chemistry, laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity.

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G. L. GOMME,
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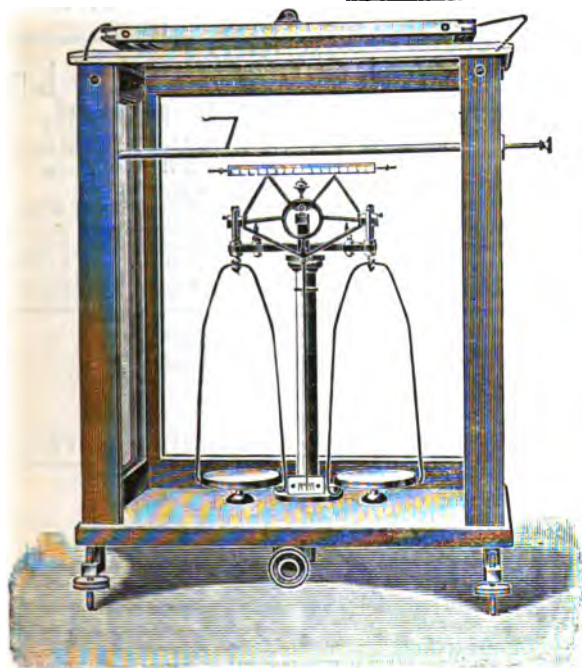
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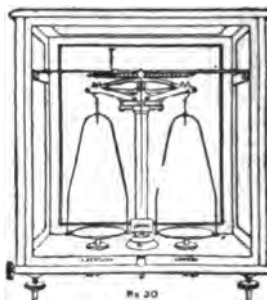
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DIAMONDS.

A LECTURE DELIVERED BEFORE THE BRITISH ASSOCIATION
AT KIMBERLEY, SEPTEMBER 5, 1905.

By Sir WILLIAM CROOKES,
Hon. D.Sc. (Oxford and Dublin), F.R.S.

If ever a man felt the real inwardness of the saying, "Carrying coals to Newcastle," it is I, who audaciously stand before you this evening. My difficulties are three-fold. I have to address an audience thickly sprinkled with experts on a subject in which I am a mere graduate. I also have to address Members of the British Association, and if possible interest them in the wonderful development of an industry which has made the few square miles in the centre of which we are standing the most valuable land on the face of the earth; and likewise I wish to illustrate the various properties of the diamond in a series of experiments few of which can be rehearsed beforehand,—as experiments sometimes destroy the stones,—and diamonds, as probably some present are aware, are expensive things.

From the earliest times the diamond has fascinated mankind. It has been a perennial puzzle—one of the "riddles of the painful earth." It is recorded in "Sprat's History of the Royal Society" (1667) that among the questions sent by order of the Society to Sir Philiberto Vernatti, Resident in Batavia, was one inquiring "Whether Diamonds grow again after three or four years in the same places where they have been digged out?" The answer sent back was "Never, Or at least as the memory of man can attain to."

In a lecture "On Diamonds," more than forty years ago Professor Maskelyne said (CHEMICAL NEWS, vol. i., p. 208):—"The diamond is a substance which transcends all others in certain properties to which it is indebted for its usefulness in the arts and its beauty as an ornament. Thus, on the one hand it is the hardest substance found in nature or fashioned by art. Its reflecting power, and refractive energy, on the other hand, exceed those of all other colourless bodies, while it yields to none in the perfection of its pellucidity." He was constrained to add "The formation of the diamond is an unsolved problem."

Of late years the subject has fascinated many men of science. The development of electricity, with the introduction of the electric furnace, has facilitated research, and I am justified in saying that if the diamond problem is not actually solved, there is every probability it shortly will be solved.

South Africa, as I will show in detail, is the favourite haunt of diamonds on this planet; it ranks with Australia and California as one of the three great gold-yielding regions. But the wealth of South Africa is not limited to gold and diamonds. It is also the illimitable home of Coal—"the Black Diamond of the Universe." The province of Natal alone contains more coal than Britain ever owned before a single bucket had been raised; and the coal beds extend into the Orange River Colony. Valuable iron ores exist also in large quantities.

In addition to these lavish natural riches the high grounds above Cape Town abound in medicinal health-giving waters. The districts where these springs occur are high lying, free from malaria, and admirably adapted for the restoration of invalids. It needs only some distinguished individual to set the fashion, some Emperor, Prince, or reigning Beauty to take the baths and drink the waters, and the tide of tourists will surely carry prosperity to Aliwal North, Fraserburg, Cradock, and Fort Beaufort.

It is to the Diamond industry I specially direct your attention to-night. I have studied diamonds scientifically for thirty years, and of the Kimberley mines I speak with the freshness of personal experience. In 1896 I spent nearly a month at Kimberley, when Mr. Gardner Williams, General Manager of the De Beers Consolidated Mines, and the Managers of neighbouring mines, did their utmost to assist me in my enquiries and to aid me with valuable information. I had free access to all the workings, above and below ground, examined at leisure their stock and took extracts from their books. I had exceptional opportunities of studying the peculiar geological formation, and of noting facts connected with the birth of the precious stone which forms the subject of this evening's lecture.

Although my experiments are chiefly connected with the physical and chemical properties of diamonds, and with researches on the perplexities of their probable formation, it will be a kind of compensation for the dryness of some theoretical points, if with the help of a few photographs—taken on my former visit to South Africa—I bring before your eyes the general character of the mines and their surroundings.

The most famous diamond mines are Kimberley, De Beers, Dutoitspan, Bultfontein, and Wessleton. Kimberley is practically in the centre of the present diamond-producing area. The mines are situated in latitude $28^{\circ} 43'$ South, and longitude $24^{\circ} 46'$ East. There are also River Washings in the neighbourhood of the Vaal river, where the work is conducted in somewhat primitive fashion. When I was at Klipdam, miners had congregated at a spot called "New Rush," where some good finds of diamonds had been reported. At one of the claims where work was proceeding vigorously I asked the proprietor to let me be present at the sorting out. He willingly consented, but no diamonds were found. On my expressing regret, he said he had not seen a diamond for a fortnight! but then he had picked out one worth £300, "and that," he said, "will pay for several weeks' wages of my boys." This is the kind of speculative gambling that goes on at the river diggings. The miner may toil fruitlessly for months, and then luckily come across a pocket of stones, swept there by some eddy, by which he will net thousands. Diamonds from the "river washings" are of all kinds, as if contributed by every mine in the neighbourhood. They are much rolled and etched, and contain a fair proportion of stones of good quality, as if only the better and larger diamonds had survived the ordeal of knocking about. Besides these mines, there are in the Orange River Colony—about 60 miles from the Kimberley diamond region—two others of some importance known as Jagersfontein and Koffyfontein, whilst about 20 miles W.N.W. of Pretoria is situated the New Premier mine, now famous as the home of the wonderful "Cullinan" diamond.

Kimberley.

The surface of the country round Kimberley is covered with a ferruginous red, adhesive, sandy soil, which makes traffic heavy. Below the red soil is a basalt, much decomposed and highly ferruginous, from 20 to 90 feet thick, and lower still from 200 to 250 feet of black slaty shale containing carbon and iron pyrites. Then deeper a bed of conglomerate about 10 feet thick, and below the conglomerate about 400 feet of a hard compact rock of an olive colour, called "Melaphyre,"* or Olivine diabase. Below the melaphyre is a hard quartzite about 400 feet thick. The strata are almost horizontal, dipping slightly to the north; in places they are distorted and broken through by protruding dykes of trap. There is no water nearer than the Vaal river, about 14 miles away; formerly the miners were dependent on rain-water and a few springs and pools. Now, however, a constant and abundant supply of excellent water is served to the town. Good brick houses, with gardens and orchards, have sprung up on all sides.

* "MELAPHYRE. A waitin' room for Rocks, till called for.

The Pipes.

The five diamond mines are all contained in a precious circle 3½ miles in diameter. They are irregular shaped round or oval pipes, extending vertically downwards to unknown depths, retaining about the same diameter throughout. They are considered to be volcanic necks, filled from below with a heterogeneous mixture of fragments of surrounding rocks, and of older rocks such as granite, mingled and cemented with a bluish coloured hard clayey mass, in which famous blue clay the imbedded diamonds are hidden.

The areas of the mines are:—

Kimberley	33 acres
De Beers	22 "
Dutoitspan	45 "
Bultfontein	36 "

Before the discovery of the mines there was nothing in the superficial appearance of the ground to indicate the priceless treasures below. Since the filling of the volcanic ducts with diamantiferous ground, denudation has planed the surface; and the upper parts of the craters and other ordinary signs of volcanic activity being smoothed away, the superficial and ubiquitous red sand has covered and disguised the whole surface. The Kimberley mine seems to have presented a slight elevation above the surrounding flat country, while the sites of other mines were level or even slightly depressed.

Other diamantiferous pipes in the neighbourhood are small and do not contain stones in payable quantities. Hoards of diamonds may await the lucky discoverer, but where there are no surface signs, and the pipe itself is hidden under 10 or 20 feet of recent deposits, prospecting is a matter of sheer speculation. Hitherto accident has been the chief factor in the discovery of diamond mines.

How the great pipes were originally formed is hard to say. They were certainly not burst through in the ordinary manner of volcanic eruption, since the surrounding and enclosing walls show no signs of igneous action, and are not shattered or broken up even when touching the "blue ground." It is pretty certain these pipes were filled from below after they were pierced, and the diamonds were formed at some previous time and mixed with a mud volcano, together with all kinds of *débris* eroded from the rocks through which it erupted, forming a geological "plum pudding." The direction of flow is seen in the upturned edges of some of the strata of shale in the walls, although I was unable to see any upturning in most parts of the walls of the De Beers mine at great depths.

The breccia filling the mines, usually called "blue ground," is a collection of fragments of shale, and of various eruptive rocks, boulders, and crystals of many kinds of minerals. Indeed, a more wildly heterogeneous mixture can hardly be found anywhere else on this globe. The Kimberley mines for the first 70 or 80 feet are filled with so-called "yellow ground," and below that with "blue ground." This superposed yellow on blue is common to all the mines. The blue is the aboriginal ground, and owes its colour chiefly to the presence of lower oxides of iron. When atmospheric influences have access to the iron it becomes peroxidised, and the ground assumes a yellow colour. The thickness of yellow earth in the mines is therefore a measure of the depth of penetration of air and moisture. The colour does not affect the yield of diamonds. The ground mass is soapy to the touch, and friable, especially after exposure to weather. Besides diamonds, more than eighty species of minerals have been recognised in the blue ground, the most common being—Magnetite, ilmenite, garnet, bright green ferrihydrous enstatite (bronzite), a hornblende mineral closely resembling smaragdite, calc-spar, vermiculite, diallage, jeffreysite, mica, kyanite, augite, peridot, iron pyrites, wollastonite, vaalite, zircon, chrome iron, rutile, corundum, apatite, olivine, sahlite, chromite, pseudobrookite, perovskite, biotite, and quartz.

The blue ground does not show any signs of igneous action; the fragments in the breccia are not fused at the

edges. The eruptive force was probably steam or water-gas, acting under great pressure but at no high temperature.

There are many such pipes in the immediate neighbourhood of Kimberley. It may be that each volcanic pipe is the vent for its own special laboratory—a laboratory buried at vastly greater depths than we have yet reached—where the temperature is comparable with that of the electric furnace, where the pressure is fiercer than in our puny laboratories and the melting-point higher, where no oxygen is present, and where masses of liquid carbon have taken centuries, perhaps thousands of years, to cool to the solidifying point. The chemist arduously manufactures infinitesimal diamonds, valueless as ornamental gems; but Nature, with unlimited temperature, inconceivable pressure, and gigantic material, to say nothing of measureless time and appalling energy, produces without stint the dazzling, radiant, beautiful, coveted crystals I am enabled to show you to-night.

This hypothesis of the origin of diamonds is in many ways corroborated.

The ash left after burning a diamond invariably contains iron as its chief constituent; and the most common colours of diamonds, when not perfectly pellucid, show various shades of brown and yellow, from the palest "off colour" to almost black. They are also green, blue, pink, yellow, and orange. These variations give support to the theory advanced by Moissan that the diamond has separated from molten iron,—a theory of which I shall say more presently,—and also explain how it happens that stones from different mines, and even from different parts of the same mine, differ from each other. Further confirmation is given by the fact that the country round Kimberley is remarkable for its ferruginous character, and iron-saturated soil is popularly regarded as one of the indications of the near presence of diamonds. Along with carbon, molten iron dissolves other bodies which possess tinctorial powers. One batch of iron might contain an impurity colouring the stones blue, another lot would tend towards the formation of pink stones, another of green, and so on. Cobalt, nickel, chromium, and manganese, all metals present in the blue ground, would produce these colours.

An hypothesis, however, is of little value if it only elucidates half a problem. Let us see how far we can follow out the ferric hypothesis to explain the volcanic pipes. In the first place we must remember these so-called volcanic vents are admittedly not filled with the eruptive rocks, scoriaceous fragments, &c., constituting the ordinary contents of volcanic ducts.

A selection of thin sections of some of these rocks and minerals, mounted as microscopic objects and viewed by polarised light, are not only of interest to the geologist, but are objects of great beauty.

The appearance of shale and fragments of other rocks testify that the mélange has suffered no great heat in its present condition, and that it has been erupted from great depths by the agency of water vapour or some similar gas. How is this to be explained?

You will recollect I start with the reasonable supposition that at a sufficient depth* there were masses of molten iron at great pressure and high temperature, holding carbon in solution, ready to crystallise out on cooling. Far back in time the cooling from above caused cracks in superjacent strata through which water† found its way. On reaching the incandescent iron, the water would be converted into gas, and this gas would rapidly disintegrate and erode the channels through which it passed, grooving a passage more and more vertical in the necessity to find the quickest vent to the surface. But steam in the presence of molten or even red-hot iron liberates large volumes of hydrogen gas, together with less quantities of hydrocarbons‡ of all

* A pressure of fifteen tons on the square inch would exist not many miles beneath the surface of the earth.

† There are abundant signs that a considerable portion of this part of Africa was once under water, and a fresh water shell has been found in apparently undisturbed blue ground at Kimberley.

‡ The water sunk in wells close to the Kimberley mine is sometimes impregnated with paraffin, and Sir H. Roscoe extracted a solid hydrocarbon from the "blue ground."

kinds—liquid, gaseous, and solid. Erosion commenced by steam would be continued by the other gases; it would be easy for pipes, large as any found in South Africa, to be scored out in this manner.

Sir Andrew Noble has shown that when the screw stopper of his steel cylinders in which gunpowder explodes under pressure is not absolutely perfect, gas escapes with a rush so overpowering as to score a wide channel in the metal. Some of these stoppers and vents are on the table. To illustrate my argument Sir Andrew Noble has been kind enough to try a special experiment. Through a cylinder of granite is drilled a hole 0.2 inch diameter the size of a small vent. This is made the stopper of an explosion chamber, in which a quantity of cordite is fired, the gases escaping through the granite vent. The pressure is about 1500 atmospheres, and the whole time of escape is less than half a second. Notice the erosion produced by the escaping gases and by the heat of friction; these forces have scored out a channel more than half an inch diameter and melted the granite along their course. If steel and granite are thus vulnerable at comparatively moderate gaseous pressure, it is easy to imagine the destructive upburst of hydrogen and water-gas grooving for itself a channel in the diabase and quartzite, tearing fragments from resisting rocks, covering the country with *débris*, and finally, at the subsidence of the great rush, filling the self-made pipe with a water-borne magma in which rocks, minerals, iron oxide, shale, petroleum, and diamonds are violently churned in a veritable witch's cauldron! As the heat abated the water vapour would gradually give place to hot water, which forced through the magma would change some of the mineral fragments into the existing forms of to-day.

Each outbreak would form a dome-shaped hill; the eroding agency of water and ice would plane these eminences until all traces of the original pipes were lost.

Actions such as I have described need not have taken place simultaneously. As there must have been many molten masses of iron with variable contents of carbon, different kinds of colouring matter, solidifying with varying degrees of rapidity, and coming in contact with water at intervals throughout long periods of geological time—so must there have been many outbursts and upheavals, giving rise to pipes containing diamonds. And these diamonds by sparseness of distribution, crystalline character, difference of tint, purity of colour, varying hardness, brittleness, and state of tension, have the story of their origin impressed upon them, engraved by natural forces,—a story which future generations of scientific men may be able to interpret with greater precision than is possible to-day.

The contents of the several pipes are not absolutely identical. The diamonds from each pipe differ in character, showing that the upflow was not simultaneous from one large reservoir below, but the result of several independent eruptions. Even in the same mine there are visible traces of more than one eruption.

The blue ground varies in its yield of diamonds in different mines.

According to tables furnished by the De Beers Company, the yield of the De Beers and Kimberley mines has declined as the depth increases. At the same time the value of the stones has risen, and diamonds are more expensive to-day than at any previous time. (See Table, next column).

The diamonds from each mine have a distinctive character, and so uniform are the characteristics that an experienced buyer can tell at once the locality of any particular parcel of stones. De Beers and Kimberley mines are distinguished by the yield of large yellowish crystals with curved edges; Dutoitspan yields mainly coloured stones, while Bultfontein—half a mile off—produces small white octahedral crystals, occasionally speckled and flawed, but rarely coloured. The diamonds from the Wesselton mine are characterised by the large number of perfect octahedra of pure water amongst them. The diamonds from the Leicester mine have a frosted, etched appearance; they are white, the crystallisation irregular ("cross-grained"), and they are hard and expensive to cut. Stones from Jagersfontein, in the Orange River

Year.	Number of carats* per load.†	Value per carat.
	s. d.	
1889	1.283	19 8.75
1890	1.15	32 6.75
1891	0.99	29 6
1892	0.92	25 6
1893	1.05	29 0.6
1894	0.89	24 5.2
1895	0.85	25 6
1896	0.91	26 9.4
1897	0.92	26 10.6
1898	0.80	26 6.2
1899	0.71	29 7.2
1900	0.67	35 10.2
1901	0.76	39 7
1902	0.76	46 5.7
1903	0.61	48 6.3
1904	0.54	48 11.8

* According to Gardner Williams the South African carat is equivalent to 3.174 grains. In Latimer Clark's "Dictionary of Metric and other Useful Measures," the diamond carat is given as equal to 3.1683 grains = 0.2053 gramme = 4 diamond grains. One diamond grain = 0.252 troy grain. 151.5 diamond carats = 1 ounce troy.

Webster's "International Dictionary" gives the diamond carat as equal to 3 1/5th troy grains.

The Oxford English Dictionary says the carat was originally 1/144th of an ounce or 3 1/3rd grains, but now equal to about 3 1/5th grains, though varying slightly with time and place.

The "Century Dictionary" says the diamond carat is equal to about 3 1/6th troy grains, and adds, that in 1877 the weight of the carat was fixed by a syndicate of London, Paris, and Amsterdam jewellers at 205 milligrammes. This would make the carat equal to 3.163 troy grains.

† A load weighs about 1600 lbs.

Colony, display great purity of colour and brilliancy and they have the so-called "steely" lustre characteristic of old Indian gems.

Let me cite a description of a visit to Kimberley in 1872, by Mr. Paterson, who gives a graphic picture of the early days.

"The New Rush Diggings (as the Kimberley mine was first called) are all going forward in an oval space enclosed around by the trap dyke, of which the larger diameter is about 1000 feet, while the shorter is not more than 700 feet in length. Here all the claims of 31 feet square each are marked out with roadways about 12 feet in width, occurring every 60 feet. Upon these roadways, beside a short pole fixed into the roadway, sits the owner of the claim with watchful eye upon the Kafir diggers below, who fill, and hoist by means of a pulley fixed to the pole above, bucketful after bucketful of the picked marl stuff in which the diamonds occur."

Soon came the difficulty how to continue working the host of separate claims without infringements. A system of rope haulage was then adopted. This mode of haulage continued in vogue during the whole of 1873, and if the appearance of the mine was less picturesque than when roadways existed, at least by moonlight it was a weird and beautiful sight.

But the mine was now threatened in two other quarters. The removal of the blue ground undermined the support from the walls of the pipe, and frequent falls of reef occurred, not only burying valuable claims but endangering the lives of workers below. Moreover, as the workings deepened, water made its appearance, necessitating pumping.

It soon became evident that open workings were doomed, and by degrees was devised the present system of underground working.

During this time of perplexity, individual miners who might have managed one or two claims near the surface could not continue work in the face of harassing difficulties and heavy expenses. Thus the claims gradually changed hands until the mine became the property first of a comparatively small number of capitalists, then of a smaller number of limited liability companies, until the whole of the mines have practically become the property of the "De Beers Consolidated Mines, Limited."

Underground Workings.

In the face of constant developments I can only describe the system in use at the time of my own visit—1896. Shafts are sunk in the solid rock at a sufficient distance from the pipe to be safe against reef movements in the open mine. In 1903, the rock shafts in the De Beers and Kimberley mines reached depths of 2076 and 2599 feet respectively. Tunnels are driven from these shafts at different levels, about 120 feet apart, to cross the mine from west to east. These tunnels are connected by two other tunnels running north and south, one near the west side of the mine and one midway between it and the east margin of the mine. From the east and west tunnels, offsets are driven to the surrounding rock. When near the rock, the offsets widen into galleries, these in turn being stoped on the sides until they meet, and upwards until they break through the blue ground. The fallen reef with which the upper part of the mine is filled sinks and partially fills the open space. The workmen then stand on the fallen reef and drill the blue ground overhead, and as the roof is blasted back the *débris* follows. When stoping between two tunnels the blue is stoped up to the *débris* about midway between the two tunnels. The upper levels are worked back in advance of the lower levels, and the works assume the shape of irregular terraces. The main levels are from 90 to 120 feet apart, with intermediate levels every 30 feet. Hoisting is done from only one level at a time through the same shaft. By this ingenious method every portion of blue ground is excavated and raised to the surface, the rubbish on the top gradually sinking and taking its place.

The scene below ground in the labyrinth of galleries is bewildering in its complexity, and very unlike the popular notion of a diamond mine. All below is dirt, mud, grime; half naked men, dark as mahogany, lithe as athletes, dripping with perspiration, are seen in every direction, hammering, picking, shovelling, wheeling the trucks to and fro, keeping up a weird chant which rises in force and rhythm when a greater task calls for excessive muscular strain. The whole scene is more suggestive of a coal mine than a diamond mine, and all this mighty organisation, this strenuous expenditure of energy, this costly machinery, this ceaseless toil of skilled and black labour, goes on day and night, just to win a few stones wherewith to deck my lady's finger! All to gratify the vanity of woman! "And," interposed a lady who heard this remark, "the depravity of man!"

With gems like diamonds, whose fabulous riches are concentrated into so small a bulk, it is not surprising that precautions against robbery are elaborate. The Illicit Diamond Buying (I.D.B.) laws are very stringent, and the searching, rendered easy by the "compounding" of the natives, is of the most drastic character. Formerly the favourite method of stealing diamonds was to swallow them, but when suspected, the personal inconveniences—in which certain powerful drugs took part—rendered this ingenious mode of stealing unpopular. It is, in fact, very difficult for a native employé to steal diamonds; were he to succeed, it would be almost impossible to dispose of them, as a potential buyer would prefer to secure the safe reward for detecting a theft rather than run the serious risk of doing convict work on the Cape Town Breakwater for a couple of years. I heard of a native who secreting a diamond worth several hundreds of pounds, after trying unsuccessfully to sell it, handed it back to the manager of his compound, glad to get the 6d. a carat to which he was entitled. Before the passing of the "Diamond Trade Act" the value of stolen diamonds reached nearly one million sterling per annum.

As a rule the better class of natives—the Zulus, Matabels, Basutos, Bechuanas—when well treated, are honest and loyal. An amusing instance was told me of the devotion of a Zulu. He had been superintending a gang of natives on a small claim at the river washings near Klipdam. The claim yielded few stones, and the owner—my informant—sold the claim, handing over the plant and small staff, our friend the Zulu continuing to look after the business when

the new man took possession. In the course of a few months the purchaser became dissatisfied with his bargain, not a single diamond having turned up since the transfer. Soon after this the Zulu came to his old master in a mysterious manner, and laying a handful of diamonds on the table, said "There, Baas, are your diamonds; I was not going to let the new man have any of them!"

Depositing Floors.

Owing to the refractory character of blue ground fresh from the mines, it has to be exposed to atmospheric influences before it will pulverise under the action of water and mechanical treatment. It is brought to the surface and spread on the floors. Soon the heat of the sun and moisture produce a wonderful effect. Boulders, hard as ordinary sandstone when fresh from the mine, commence to crumble. At this stage the treatment of the diamonds assumes more the nature of farming than mining. To assist pulverisation by exposing the larger pieces to atmospheric influences, the ground is frequently harrowed and occasionally watered. The length of time necessary for crumbling the ground preparatory to washing depends on the season of the year and the amount of rain. The longer the ground remains exposed the better it is for washing. When the process is complete the softened friable blue clay is again loaded into trucks and taken to the washing machinery, where it is agitated with water and forced through a series of revolving cylinders perforated with holes about an inch in diameter; incorrigible lumps that will not pass the cylinders are again either subjected to the weathering process or passed between crushing rollers.

If a miner sees a diamond in a truck or in any of the blue ground in the mine, he has orders to secure it, and when he comes to the surface report it to the manager of the compound. If a white labourer, he is then credited with 3s. a carat, and if a black 6d. a carat. For a diamond found on the depositing floors about half these sums are paid.

Washing and Concentrating Machinery.

The fine ground which has passed through the holes in the cylinder, together with a plentiful current of water, flows into the washing pans. These pans are of iron, 14 feet in diameter, furnished with ten arms, each having six or seven teeth. The teeth are set to form a spiral, so that when the arms revolve the teeth carry the heavy deposit to the outer rim of the pan, while the lighter material passes towards the centre and is carried from the pan by the flow of water. The heavy deposit contains the diamonds. It remains on the bottom of the pan and near its outer rim. This deposit is drawn off every twelve hours by means of a broad slot in the bottom of the pan. The average quantity of blue ground passed through each pan is from 400 to 450 loads in ten hours. The deposit left in each pan after putting through the above number of loads amounts to three or four loads, which go to the pulsator for further concentration.

The Pulsator.

The Pulsator is an ingeniously designed, somewhat complicated machine for dealing with the diamantiferous gravel already reduced one hundred times from the blue ground; the pulsator still further concentrating the gravel till the precious stones can be picked out by hand. The value of the diamonds in a load of original blue ground is about 30s., the gravel sent to the pulsator from the pans, reduced a hundred-fold, is worth £150 a load.

Mr. Fred Kirsten, an employé of the De Beers Company, made in 1897 the remarkable discovery that diamonds alone, of all minerals contained in the blue ground, adhere to grease, that all others will flow away as tailings over the end of the percussion table with the water. Now all the sorting (except for the very coarse size) is done by these machines.

* Specification of G. Labram, of Kimberley, for "A Method and Apparatus for Separating Diamonds from Earthy Matters." 24,504/97.

whose power of distinction is superior to the keenest eye of the native.

The diamond has a peculiar lustre, and on the sorter's table it is impossible to mistake it for any other stone. It looks somewhat like clear gum arabic, with a sort of intrinsic lustre which makes a conspicuous shine among the other stones.

Sometimes as many as 8000 carats of diamonds are separated in one day, representing about £10,000 in value.

About two million carats of diamonds are turned out of the Kimberley mines in a year, and by the end of 1904 ten tons of diamonds had come from these mines, valued at £60,000,000 sterling. This mass of blazing gems could be accommodated in a box five feet square and six feet high.

The diamond is a luxury for which there is only a limited demand. Ten years ago, from 4 to 4½ millions sterling were spent annually in diamonds. The last few years there has been no necessity to restrict the supply, and at the mines of the De Beers Company there is no keeping pace with the demand.

Prodigious diamonds are not so uncommon as is generally supposed. Diamonds weighing over an ounce (151·5 carats) are not unfrequent at Kimberley. Nine years ago, in one parcel of stones I saw eight perfect ounce crystals, and one inestimable stone weighing two ounces. The largest diamond from the Kimberley mines weighed 428½ carats, or nearly 4 ounces troy. It measured 1½ inch through the longest axis, and was 1½ inch square. After cutting, it weighed 228½ carats, losing 200 carats in the process. The largest known diamond has recently been discovered at the New Premier mine, about 20 miles W.N.W. of Pretoria. This mine is of the same type as the Kimberley mines, but much larger in size, and in fact it is the largest known diamantiferous pipe in the world,—the pipe containing the "blue ground" along the longer diameter of its oval-shaped cross-section measuring over half a mile, the area of which is estimated at 350,000 square yards. This pipe breaks through felsitic rocks. The diamond, called "Cullinan" from the name of one of the directors of the Company on whose farm it was discovered, weighs no less than 3025½ carats, or 9586·5 grains (1·37 lbs. avoirdupois). It is a fragment, probably less than half, of a distorted octahedral crystal; the other portions still await discovery by some fortunate miner. Through this unequalled stone I passed a beam of polarised light in various directions, and could see colours in all cases, the brightest appearing when the light passed along the greatest diameter—about four inches. Here the colours were very fine, but no regular figure was to be seen. These observations show that the diamond is in a state of internal strain.

The clearness throughout is remarkable, the stone being absolutely limpid like water, with the exception of a few flaws, dark graphitic spots, and coloured patches close to the outside. At one part near the surface there is an internal crack, showing well the colours of thin plates. At another point there is a milky, opaque mass, of a brown colour, with pieces of what may be iron oxide. There are four cleavage planes of great smoothness and regularity. On other parts of the surface the crystalline structure is very marked. The edges are rounded in parts, and triangular markings (depressions) are to be seen. I also noticed square depressions, nearly as sharp and perfect as the triangular ones. Gigantic as is the Cullinan diamond, it represents in weight less than half the daily output of the De Beers mines, which averages about 7000 carats per day.

Next in size to the "Cullinan" comes the one which was found at the Jagersfontein mine. It weighed 970 carats—over half a pound.

I will show you on the screen the relative sizes of some large or famous diamonds.

1. Koh-i-noor, after the second cutting, 106 carats.
2. Loterie d'Angleterre, 49 carats.
3. Nizam of Hyderabad, 279 carats.
4. Orloff, 194 carats.
5. Koh-i-noor, after first cutting, 279 carats.
6. Regent or Pitt, 137 carats.

7. Duke of Tuscany, 133 carats.
8. Star of the South, 124 carats.
9. Pole Star, 40 carats.
10. Tiffany, yellow, 125 carats.
11. Hope, blue diamond, 44 carats.
12. Sancy, 53 carats.
13. Empress Eugénie, 51 carats.
14. Shah, 86 carats.
15. Nassak, 79 carats.
16. Pacha of Egypt, 40 carats.
17. The Cullinan, 3025 carats.
18. Excelsior, Jagersfontein, 969 carats.

The Diamond Office.

From the sorting room the stones are taken to the Diamond Office to be cleaned in acids and sorted into classes by the valuers, according to colour and purity. It is a sight for Aladdin to behold the valuers at work in the strong-room of the De Beers Company. In the Kimberley treasure store the tables are literally heaped with stones won from the rough blue ground—stones of all sizes, purified, flashing, and of inestimable price; stones coveted by men and women all the world over; and last but not least stones that are destined to largely influence the development and history of a whole huge continent.

The Compound System

One great safeguard against robbery is the "compound" system of looking after the natives. A "compound" is a large square, about 20 acres, surrounded by rows of one-storey buildings of corrugated iron. These buildings are divided into rooms each holding about twenty natives. Within the enclosure is a Store where the necessities of life are supplied at a reduced price, and wood and water free of charge. In the middle is a large swimming-bath with fresh water running through it. The rest of the space is devoted to games, dances, concerts, and any other amusement the native mind can desire. In case of accident or illness there is a well-appointed hospital where the sick are tended. Medical supervision, nurses, and food are supplied free by the Company.

In the compound are to be seen representatives of nearly all the picked types of African tribes. Each tribe keeps to itself, and to go round the buildings skirting the compound is an admirable object-lesson in ethnology. At one point is a group of Zulus; next we come to Fingoes; then Basutos; beyond come Matebele, Bechuanas, Pondos, Shangains, Swazis, and other less known tribes, either grouped or wandering around making friendly calls.

The clothing in the compound is diverse and original. Some of the men are evident dandies, whilst others think that in so hot a climate a bright coloured handkerchief or "a pair of spectacles and a smile" is as great a compliance with the requirements of civilisation as can be expected.

The natives are not interfered with in their various amusements, always provided they do not make themselves objectionable to their neighbours. They soon learn that tribal animosities are to be left outside the compound. One Sunday afternoon my wife and I walked unattended about the compound, almost the only whites present among 1700 natives. The manners of the fold were so friendly, and their smiles so cordial, that the idea of fear vanished. At one part a Kaffir was making a pair of trousers with a bright nickel-plated sewing-machine, in which he had invested his savings; next to him a "boy" was reading from the Testament in his own language to an attentive audience; in a corner a party were engaged in cooking a savoury mess in an iron pot; further on the orchestra was tuning up, and Zulus were putting the finishing touches to their toilet of feathers and beads. One group was intently watching a mysterious game. It is played by two sides, with stones, and grooves and hollows in the ground, and appears of most absorbing interest. It seems to be universal throughout Africa; it is met with among the ruins of Zimbabwe, and signs of it are recorded on old

Egyptian monuments. I wanted to learn it, and an intelligent Zulu player offered to teach it to me in a few minutes. Captain Dallas, however, with a more accurate opinion of my sharpness than my friend the Zulu, assured me it would take months of study before I could begin to know anything about it. He had tried for years, and could make nothing of it.

They get good wages, varying according to occupation. The work is appreciated, and there are always more applicants than can be accepted. On entering, the restrictions to which they must submit are fully explained, and they are required to sign for three months at least, during which time they must not leave the compound or mine. It is seldom that a man does not return, once he has lived the life in the compound; some come again and again for years, only leaving occasionally to spend accumulated savings. The most careful men save money, and carry it at intervals to the superintendent to keep for them. Occasionally they ask to look at their savings, which may amount to £30 or £40, accumulated by dribbles. They are ignorant of savings banks or interest, and are content if they see their own money in the original rags and papers in which it was handed in. The Kaffir, on demand, must behold his coins just as he handed them in, wrappings and all. Sometimes the superintendent will have as much as £1000 of savings in his care.

(To be continued).

THE DETECTION OF METHYL ALCOHOL.*

By HEYWARD SCUDDER.

THE tests for the detection of methyl alcohol are used chiefly to distinguish it from ethyl alcohol, so their value is dependent first on a sharp distinction from ethyl alcohol, then on their delicacy and rapidity. In the following description the standard of delicacy will be taken as the quantity of methyl alcohol that can be detected in ethyl alcohol. Most of the tests will show very much smaller quantities of methyl alcohol in water, but their use for such a purpose is practically unknown.

Odour Tests.

This is made by adding to the solution salicylic acid and concentrated sulphuric acid and warming, thus forming methyl salicylate, which is supposed to have a characteristic odour (of oil of wintergreen). In experiments made on eight persons I found that none of them could distinguish between ethyl and methyl alcohol by this test, because the odour of ethyl salicylate so strongly resembles that of methyl salicylate. If told that both alcohols were present a difference in odour was often noticed, but if solutions of unknown content were given, e.g., two tubes of methyl or two of ethyl alcohol, the test failed even when comparative tests with the alcohols were made.

All tests dependent on odour are unsatisfactory, because it is impossible to make accurate comparative tests. After smelling any odorous body, probably on account of persistence of the odour in the nasal passages, or possibly from slow reactivity of the olfactory nerves, it is not possible for an ordinary person to have an accurate perception of the odour of a second body. This can readily be shown experimentally, most surprising mistakes being made after the sense of smell is once blunted. In making colour tests the comparison is direct and the subjective effect of memory is eliminated.

I have been told that this test has been used in trials, for adulteration of liquors, to show juries the difference between the two alcohols, the point being made that there is a difference in the rapidity of the production of the odour as well as in the quality. I consider the test unre-

liable and not sufficiently rapid to be an improvement on the test by oxidation with a hot copper spiral and testing for the oxidation product by resorcin. The difference in colour between the condensation products of acetaldehyde and resorcin and formaldehyde and resorcin is great enough to be appreciated by any juror.

(Sieker, *Pharm. Review*, 1901, xix., 19, 117, and Chozek, *Farmas. Westnik*, lxxxix., 167—abstract *Frs. Zeit.*, 1905, xlv., 44, 124, give tests for methyl alcohol depending on the recognition of the odour of formaldehyde after oxidation. They recommend the test for use in the case of drugs, &c., where many compounds are present. The tests are not very delicate).

Colour Tests.

In the Riche and Bardsy (*Comptes Rendus*, 1875, lxxx., 1076), test the methyl alcohol is converted into methyl aniline, which is then tested for. The test is too long and slow to be of much use to-day.

In all the other tests the alcohol is oxidised to formaldehyde, methylal, or formic acid. The colour test is then applied to this oxidation product. Methylal gives the same reaction as formaldehyde in almost all tests. If ethyl alcohol is present, either the colour test must be given only by the oxidation product of methyl alcohol as in oxidation to the acid, formic acid giving a dark colour with silver nitrate, while acetic acid gives no colour—or enough of the corresponding oxidation product of ethyl alcohol must be removed to prevent interference with the colour. The difficulty of fulfilling these conditions is the chief cause of failure in the tests used. It is practically impossible to control oxidation so as to get a good yield of formic acid, and the tests for its detection are not very delicate. The removal of all the acetaldehyde without some loss of formaldehyde is impossible, but this method is perfectly practicable since the tests for formaldehyde are extremely delicate. The fact that pure ethyl alcohol when oxidised by any of the methods used in the tests for methyl alcohol gives some formaldehyde, is not sufficiently considered. It has been shown (Mulliken, Scudder, *Am. Chem. Journ.*, 1900, xxiv., 446) that when ethyl alcohol is oxidised by a heated copper spiral, formaldehyde is formed in small amounts. I have found that this is also true when ethyl alcohol is oxidised in cold dilute solution by potassium bichromate and sulphuric acid, or by potassium permanganate and sulphuric acid, enough formaldehyde being made to give the gallic acid test.

Therefore, it is obvious that the test used to show the presence of formaldehyde, after oxidation of the alcohol, must not be too delicate, or it will apparently show the presence of methyl alcohol when none is really there. This is the defect of the gallic acid reaction,* an extremely characteristic test for formaldehyde and one little obscured by the presence of other compounds, but so delicate that it is given by solutions of ethyl alcohol, cane-sugar, and a great variety of compounds after oxidation by a heated copper spiral (Mulliken, Brown, and French, *Am. Chem. Journ.*, 1904, xxv., 115).

The tests that follow are grouped by the reagent used for the production of the colour, in order to make more clear a general understanding of the difficulties and of the sources of error.

Reagent, Silver Nitrate.

Miller Test (Allen's "Commercial Organic Analysis," 3rd Ed., vol. i., p. 81).—This consists in oxidation in the cold by potassium bichromate and sulphuric acid, distillation, and testing the distillate for formic acid by silver nitrate. Allyl alcohol and acetone are said to give the same reaction. It is noted that a trace of formic acid or some other reducing agent is formed from ethyl alcohol. The test is not delicate and is of little importance.

* The solution to be tested is mixed with 0.2 c.c. of a saturated alcoholic solution of gallic acid and poured on top of (not mixed with) concentrated sulphuric acid in a test-tube. A contact ring of blue or green and blue shows the presence of formaldehyde.

* Presented before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, July, 1905.

Reagent, Lead Peroxide.

Trillat Test (*Ann. Chim. Anal. Appl.*, 1899, iv., 42; *Comptes Rendus*, 1899, cxxviii., 438; *Bull. Soc. Chim.*, [3], 1899, xxi., 445).—This consists in oxidation in cold dilute solution by potassium bichromate and sulphuric acid, under which conditions methyl alcohol is said to give methylal, ethyl alcohol to give acetaldehyde, acetal, and acetic acid. The acetaldehyde is removed by distilling 25 c.c. The next 100 c.c. distilled contain the methylal. One-half of this is digested in a closed flask with dimethylaniline at 70–80° for three hours, forming tetramethyldiaminodiphenylmethane. The solution is made alkaline and the excess of the dimethylaniline distilled off. The residue is acidified by acetic acid and a little lead peroxide added. On boiling, a blue colour appears if methyl alcohol is present. It is said to show 0.2 per cent methyl alcohol in ethyl. The time required for the test is about five hours.

The difficulties are numerous. If all the acetaldehyde is not removed by the fractional distillation, what remains may give a colour that resembles or interferes with that from methylal. Since some methylal distils over with the acetaldehyde it is not safe to distil off much more than 25 c.c. to remove the latter, for if only a small amount of methyl alcohol is present, the loss might be sufficient to spoil the test. The dimethylaniline and the lead peroxide must be very pure or the colour may be affected. In distilling off the excess of dimethylaniline (this procedure is necessary because dimethylaniline gives a violet or blue colour with lead peroxide) some methylal is lost, as may be shown by tests. I have found it easy to be sure of the removal of all the dimethylaniline, by filtering through a wet filter before distilling. No special care is necessary in acidifying after the removal of the dimethylaniline, since a great excess of acetic acid has no effect on the colour. The amount of lead peroxide used is actually a variable quantity. The directions call for four to five drops of a suspension in water. In addition to the variable strength of different samples, another error is possible here, since the amount of lead peroxide present will depend on how thoroughly the suspension is shaken before use. If too little is used, the colour is faint. If too much is used, the colour changes from blue to brown, though the effect of heat in deepening the colour still persists.

The depth of colour is supposed to be proportional to the amount of methyl alcohol originally present, but it is sometimes difficult to get this result. I have found a much fainter colour from a solution that contained 10 per cent of methyl alcohol than from one that contained 1 per cent, though the procedure was the same in each case.

I believe that the development or deepening of the colour by boiling is characteristic. Acetaldehyde, after digestion with dimethylaniline and subsequent treatment as in the Trillat test, gives in the cold a colour varying from green-yellow to green-blue. Dimethylaniline in the cold gives with lead peroxide a colour varying from green-yellow to pure blue. But in both cases the colour does not deepen on boiling, while the blue from methyl alcohol develops only on boiling. The colour may be diminished or changed by the use of the wrong amount of lead peroxide, but here again boiling makes a characteristic deepening, if methyl alcohol was in the original solution tested, so that if there is a colour in the cold that disappears or is not deepened by boiling, no methyl alcohol is present (provided the test has gone well). If the colour deepens on boiling, even if it is not a pure blue but possibly a green-blue or brown, methyl alcohol is present.

Wolf (*Ann. Chim. Anal. Appl.*, 1899, iv., 183) states that pure ethyl alcohol gives the same reaction as methyl when the Trillat test is used, but that if the digestion with dimethylaniline is made at room temperature for twenty-four hours instead of at 70–80° for three hours the test works perfectly. He claims that 0.1 per cent of methyl alcohol can be shown in ethyl alcohol in this way. Since he makes no statement of the effect of heat on the colour, the value of the improvement is doubtful, for it is possible

that the colour obtained from ethyl alcohol was due to the incomplete removal of acetaldehyde.

Robine* gives an elaborate criticism of the Trillat test, and suggests several small changes in the procedure. His most essential points are the recommendation to make a blank test of every fresh sample of dimethylaniline; the necessity for having pure lead peroxide and for using the proper amount; the difficulty of removing all the acetaldehyde without loss of methylal; and the fact that the test is spoiled unless all the acetaldehyde is removed. The presence of acetaldehyde is sometimes indicated by a yellow colour of the solution and a precipitate of aldehyde resin after the excess of dimethylaniline has been distilled off. His criterion for the presence of methyl alcohol is that the final test must give a pure blue appearing hot, disappearing cold. Any shade of blue that has green in it, green-yellow, or pure green, is not to be regarded, since it may come from incomplete removal of acetaldehyde.

Since Robine notes the effect of heat on the colour, it would appear probable that he tried heating in the cases where the colour was due to acetaldehyde, but the fact that in such cases no deepening occurs when the solution is boiled is not mentioned by him. This differs from my observations previously given.

It is evident that the Trillat test must be used with care. It is delicate and fairly rapid, but the test may be spoiled not only by slight variations in the procedure, but also by causes of unknown origin which occur when the procedure is strictly followed. It is certainly not a test to be recommended to persons of limited knowledge of chemistry.

(To be continued).

THE FORMATION OF OZONE BY ULTRA-VIOLET LIGHT.

By FRANZ FISCHER and FRITZ BRAEHMER.

LENARD (*Ann. Phys.*, 1900, i., 486) first observed that ultra-violet light is capable of ozonising oxygen. When he allowed the light of a spark-gap to act upon oxygen through a quartz plate (transparent to ultra-violet) ozone was formed. But no ozone was formed if the light had also to penetrate a sheet of mica (opaque to ultra-violet).

Goldstein (*Berichte*, 1903, xxxvi., 3042) noticed a smell of ozone outside Geissler tubes as soon as a discharge was sent through them, but only if they were partly made of quartz. He regarded this as an effect of ultra-violet light, and it is very probable that the ozone, which he condensed by means of liquid air in the interior of his tubes, thus in the region of electric discharge, owes its formation to ultra-violet radiation.

Warburg (*Ann. Phys.*, 1904, xiii., 475) has shown that during the so-called silent electric discharge, e.g., in Siemens' ozone tubes, ultra-violet light and cathode rays appear, and it seems to him that the cause of the formation of ozone is to be found in the appearance of these rays.

Warburg and Regener (*Sitzungsber. Preuss. Akad. d. Wiss.*, 1904, 1228) allowed the ultra-violet light of a spark-gap to act upon pure oxygen in the quartz capillary of their differential ozonometer, and measured the contraction of volume. They also allowed the rays to act upon strongly ozonised oxygen, and determined its increase of volume. From their measurements they conclude that besides an ozonising radiation, disozonising rays are also at work, and their curves for ozonisation and disozonisation intersect at 2.2 per cent ozonisation; i.e., under Warburg and Regener's conditions at 2.2 per cent ozonisation the rates of formation and decomposition are equal.

For our purpose, i.e., the determination of the conditions of formation and the relative yields on ozonising oxygen

* *Ann. Chim. Anal. Appl.*, 1901, vi., 128, 171; cf. Huler (*Ber.*, 1904, xxxvii., 3411) and Bach (*ibid.*, 1904, xxxvii., 3986) on the unreliability of the Trillat test for formaldehyde, which is the same as the methyl alcohol test beginning with the digestion with dimethylaniline.

by ultra-violet light, the quartz mercury arc lamp, which is rich in ultra-violet rays, seemed to us specially suitable (A. Pflüger, "Die Quecksilberlampe als Ultra-violette Lichtquelle," *Phys. Zeit.*, 1904, v., 414; Ladenburg, "Spectrale Energieverteilung der Quecksilberlampe aus Quarzglas," *Phys. Zeit.*, 1904, v., 525); it is already known that its radiation ozonises the air. We used for this purpose a lamp of the form previously described by one of us (*Berichte*, 1905, xxxviii., 2630).

Pure oxygen was used for the investigation. This was prepared electrolytically from dilute sulphuric acid, was led through glass-wool and then over heated platinised asbestos, so that any admixed ozone in it was destroyed and traces of hydrogen were oxidised to water. Then the oxygen passed into a so-called intensive washing flask with concentrated sulphuric acid, and then entered the quartz vessel of the mercury lamp between the second quartz wall and the glass condenser cooled with water. The oxygen containing ozone left the lamp through the middle of the glass condenser.

In an absorption apparatus, closed by means of mercury, iodine was separated out from neutral potassium iodide solution by means of the ozone. In all experiments the procedure adopted was the same. In the absorption tube 20 c.c. of $N/10$ potassium iodide solution were placed; it was always washed out with the same volume of water, acidulated with 20 c.c. of $N/10$ sulphuric acid solution, the same volume of starch solution of constant concentration added, and the iodine separated was finally titrated with $N/10$ sodium thiosulphate solution.

The lighting of the lamp was effected by means of a small inductor. The discharge space of the lamp was permanently connected with a mercury air-pump, and the vacuum was regulated partly by means of this and partly by means of an absorption tube which contained ignited carbon, and was placed in liquid air.

The following are the chief points which were considered in this research:—

1. Effect of cooling the gas.
2. Influence of strength of the light of the lamp.
3. Influence of the velocity of the current of gas.
4. Influence of the degree of purity of the gas.

1. Effect of Cooling the Gas.

In consequence of the rapidly increasing rate of destruction of the ozone with rising temperature (Clement, "Bildung des Ozons bei Hoher Temperatur," *Ann. Phys.*, 1904, xiv., 334) it was to be expected that the cooling of the gas exposed to the rays of the lamp would have a considerable effect upon the obtainable concentration of the ozone.

If we led the gas without any cooling through the lamp, at the same time allowing no water to flow through the glass condenser, no appreciable amount of ozone was obtained.

The measurement of the temperature, which was quickly produced as soon as the vessel was closed, although the quartz vessel had double walls and the space between the two walls was carefully exhausted, afforded an explanation. We found a minimum temperature of 270° , at which temperature it has long been known that ozone cannot exist. But if water was sent through the condenser, the gas, passing through the narrow space (1 m.m. wide) between the inner warmed quartz wall and the outer wall of the glass condenser which was kept cold, cooled the quartz wall, and very considerable quantities of ozone were found.

(a) *Effect of the Velocity of the Water.*—In Table I. the cooling water at 15° possessed only two-thirds of the velocity in Table II. The tables give under "No." the number of the experiment, under "A.L." and "A.E." the current strength in the lamp and the electrolyser producing oxygen respectively; under "titration" are given the c.c. of $N/10$ thiosulphate which were needed to titrate the iodine separated by the ozone, under "Mg. O_3 " the amount of ozone calculated from this, and under "weight per cent

O_3 " the percentage of ozone present in the oxygen. For this the total weight of the oxygen was calculated from the current strength in the electrolysing apparatus. The experiments always lasted fifteen minutes.

TABLE I.

No.	A.L.	A.E.	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5·1	3·01	1·69	0·406	0·182
2.	5·1	3·01	1·80	0·432	0·193
3.	5·1	3·01	1·81	0·434	0·194

TABLE II.

No.	A.L.	A.E.	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5·1	3·01	2·03	0·487	0·217
2.	5·1	3·01	2·05	0·492	0·219
3.	5·1	3·01	2·06	0·494	0·221

Comparison of Tables I. and II. shows that with increasing velocity of the cooling water, i.e., increased cooling, the amount of ozone formed increases, so that if the strength of the gas current remains the same the percentage becomes greater.

(b) *Effect of the Temperature of the Water.*—In order to determine the influence of the temperature directly, the water was forced at a constant weight through the glass condenser by means of a pump driven by an electro-motor. The circulation of the water was as follows:—From the pump it passed through an externally cooled lead pipe through a vessel with thermometer 1, through the glass condenser, through a vessel with thermometer 2, and back to the pump. T_1 and T_2 give the temperatures of the water before entering and after leaving the glass condenser respectively. The velocity of the water was considerably less than that of the condenser water.

TABLE III.—Lead Tubing Cooled Externally by Water at the Temperature of the Room.

No.	A.L.	A.E.	T_1 .	T_2 .	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5	3	21·5°	22·5°	1·35	0·324	0·145
2.	5	3	22	23	1·61	0·386	0·173
3.	5	3	22	23	1·62	0·389	0·174

TABLE IV.—Lead Tubing Cooled Externally with Ice.

No.	A.L.	A.E.	T_1 .	T_2 .	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5	3	+1°	+2°	1·81	0·434	0·194
2.	5	3	+1	+2	1·79	0·430	0·192
3.	5	3	+1	+2	1·81	0·434	0·194

TABLE V.—Calcium Chloride Solution used in the Circuit instead of Water. Lead Tubing Cooled Externally by means of a Cooling Mixture.

No.	A.L.	A.E.	T_1 .	T_2 .	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5	3	-10°	-2·5°	2·27	0·545	0·244
2.	5	3	-10	-2·5	2·4	0·576	0·258
3.	5	3	-10	-2·5	2·21	0·530	0·237

Comparison of Tables III., IV., and V. shows clearly the influence of the temperature of the cooling liquid. As the temperature falls the percentage of gas rises considerably.

As the lamp burns under water, it does not appear possible that the increased cooling in the glass condenser has any appreciable cooling effect upon the lamp, and thus influences the nature of the light emission in a manner favourable to the formation of ozone.

2. Influence of the Strength of the Light.

The cooling was kept constant, and also the current of the gas (as far as possible), and the current through the lamp—and hence the strength of the light—was varied. The potential of the lamp amounted to, roughly, 20 volts.

Thus at first the yield of ozone increases with increasing strength of light, but finally decreases. In our opinion, the decrease is due to the fact that finally, as the current through the lamp goes on increasing, the temperature is raised too high, and then the rate of decomposition of the ozone formed assumes appreciable values.

TABLE VI.

No.	A.L.	A.E.	Titration.	Mg.O ₂ .	Weight per cent O ₂ .
1.	2	2'06	1'68	0'403	0'183
2.	2	2'99	1'68	0'403	0'181
3.	3	3'01	2'00	0'480	0'214
4.	3	3'00	2'00	0'480	0'215
5.	6'5	3'00	2'09	0'502	0'224
6.	6'5	3'00	2'10	0'504	0'226
7.	8	3'00	2'02	0'485	0'217
8.	8	3'00	2'04	0'490	0'219

3. Influence of the Strength of the Gas Current.

The cooling effect of the gas upon the quartz wall we have already mentioned. It was therefore to be expected that, on increasing the velocity of the gas current, the absolute quantity of ozone produced would be increased—firstly, because the cooling effect upon the quartz wall would be increased; and, secondly, because the ozone, being more quickly removed, would be protected from warming and thus from decomposition. The percentage of ozone in the gas, however, would probably be decreased. Table VII. confirms our suppositions.

TABLE VII.

No.	A.L.	A.E.	Titration.	Mg.O ₂ .	Weight per cent O ₂ .
1.	5	2'03	1'59	0'382	0'253
2.	5	2'06	1'59	0'382	0'249
3.	5	3'09	2'20	0'528	0'230
4.	5	3'10	2'25	0'540	0'234
5.	5	3'95	2'47	0'593	0'201
6.	5	4'00	2'38	0'571	0'192

Thus we see that, on doubling the strength of the gas current (from 2 to 4 ampères), the absolute amount of ozone produced by the lamp is also nearly doubled, while, on the other hand, the percentage amounts to only four-fifths of the first percentage. Whether on further increasing the strength of the gas current the yield is also proportionately increased is not yet known.

4. Influence of the Purity of the Oxygen.

We have finally allowed our pure oxygen to contain different amounts of water-vapour, drying it once only with calcium chloride and the other time with concentrated sulphuric acid. For the present, however, we cannot report any definite results.

On the basis of the preceding results we may summarise as follows:—

The ozonisation of oxygen by means of ultra-violet light results if the temperature of the gas is not too high. Practically it does not occur at all if the gas has a temperature above 270°, because then the reaction $3O_2 \rightleftharpoons 2O_3$, in consequence of the supply of heat, proceeds from right to left more rapidly than it goes from left to right, in consequence of the absorption of the energy of ultra-violet light. These results agree with those of Clement (*loc. cit.*) from the Nernst Institute, according to which the rate of decay of ozone rapidly increases with increasing temperature. They also explain the fact that, with Heraeus' quartz mercury lamp, for example, the smell of ozone decidedly decreases soon after the lamp has been lighted. The ozone forming on that lamp's simple quartz wall, which becomes hot, again decomposes in consequence of the heat, so that very little ozone is formed near the hot quartz. The gradually occurring alteration in the spectral distribution of the light might indeed act in the same way.

The effects of the strength of the light of the lamp, which have been repeatedly confirmed, and also of the cooling and velocity of the gas current, agree perfectly with what is known concerning the influence of the silent electric discharge on ozone formation, for example, in Siemens' ozone apparatus, and seem to be a proof of the correctness of Warburg's view (*loc. cit.*) that the formation of ozone by the silent electric discharge is due to the ultra-violet light thus formed.

A short time ago one of us showed that the lamp used by us can produce in a few hours the violet colouration of glass containing manganese, which is effected by sunlight in high mountainous regions in months and years, and in our low regions only after longer periods, because the ultra-violet part of its spectrum is strongly absorbed by the earth's atmosphere.

By this absorption of ultra-violet sunlight by our atmosphere, as is universally accepted on the basis of Lenard's observations (*loc. cit.*), ozone results in the upper layers of air; when it sinks to lower regions it is decomposed by oxidisable substances.

We are at present engaged in altering our apparatus in order to free ourselves more from the disturbing effects of the radiation of heat. As we require some time for this purpose, we publish here the results we have obtained up to the present. As far as we can see from preliminary experiments, the yield of ozone is capable of being considerably increased.—*Berichte*, 1905, xxxviii., 2633.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 7, August 14, 1905.

The Gases Evolved from Actinium.—A. Debiere.—The author performs a large number of experiments with a solution of radium bromide and with salts of actinium, both in solution and in the solid state, and finds that helium is evolved on heating both sets of salts. The gaseous mixture evolved is introduced into a glass tube containing different substances for absorbing all the gases which react chemically. Thus the oxygen, hydrogen, gaseous carbides, and nitrogen, besides other compound gases, are got rid of, leaving only the gases of the argon group. These are transferred into a small capillary tube with two electrodes and the spectrum photographed and examined. It is evident from the control experiments performed by the author that the helium results from the presence of the radio-active bodies.

The Dense Liquids containing Alkaline Iodo-mercurate Bases.—M. Duboin.—The author investigates the heavy liquid consisting of a saturated solution of mercury iodide in a solution of potassium iodide. He then attempts to prepare still heavier liquids by replacing the potassium iodide by other alkaline iodides—those of sodium, lithium, and ammonium. The density of potassium iodo-mercurate is 3'196 at 22'9°; of sodium iodo-mercurate solution, 3'46 at 26°; of lithium iodo-mercurate solution, 3'28 at 25'6°; and of ammonium iodo-mercurate, 2'98 at 26°. The liquid containing the sodium salt gives with excess of water a dense precipitate of mercuric iodide, which dissolves without decomposition in alcohol. Owing to this fact, the sodium iodo-mercurate solution is very useful for the separation of minerals and determination of their densities. This compound also dissolves without decomposition in a large number of organic liquids, such as methylic and ethylic alcohols, ethylic and benzylic aldehydes, acetone, formic, acetic, propionic, butyric, and valeric acids, besides ethyl acetate and oxalate.

Nos. 8 and 9, August 21 and 28, 1905.

These two numbers contain no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 11, 1905.

Hydrolysis of Tin Chloride and Bromide.—P. Pfeiffer.—If tin tetrachloride is dissolved in water, ether added, and the ethereal layer evaporated, a white crystalline mass is obtained. Analysis shows that these crystals have the composition represented by the formula

$\text{SnCl}_3\text{OH} + \text{H}_2\text{O} + (\text{C}_2\text{H}_5)_2\text{O}$. The corresponding bromide compound can be prepared similarly. These compounds are undoubtedly the intermediate products of the hydrolysis of the tetrachloride and tetrabromide respectively. The "alcoholysis" of the tin halides proceeds similarly in its first stages, $\text{SnCl}_3\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$ being formed. Since tin tetrachloride is not an electrolyte, and alcohol possesses only a very small power of dissociating dissolved substances, the process in both hydrolysis and alcoholysis is purely chemical, and is to be explained without the aid of ionic reactions. In the author's opinion, when tin tetrachloride (or tetrabromide) reacts with water, hydrates are first formed, which then in presence of excess of water give up hydrochloric (or hydrobromic) acid, and yield the

intermediate product, $\text{Sn} \begin{smallmatrix} \text{Cl}_3 \\ (\text{OH}_2)_x \end{smallmatrix} \rightarrow \text{SnOH} \begin{smallmatrix} \text{Cl}_2 \\ (\text{OH}_2)_{x-1} \end{smallmatrix}$. By the repetition of this process stannic acid is finally produced.

Ultramarine Blue.—K. A. Hofmann and W. Metzner. —Although ultramarine, unlike other blue dyes, is rapidly decomposed by dilute acids or solutions of salts with acid reactions, it is perfectly stable in presence of concentrated sulphuric acid or glacial acetic acid. Thus ultramarine S may be kept in a closed flask with 98.5 per cent sulphuric acid for six weeks at ordinary temperatures without suffering the least change of colour; with 93 per cent acid a change begins to occur after twelve hours, and with 89 per cent acid after three hours. Fuming sulphuric acid does not affect ultramarine blue at ordinary temperatures, and, moreover, protects it against the action of fuming nitric or nitrous acid, which would otherwise oxidise the sulphur group. On investigating quantitatively the behaviour of ultramarine with acetic acid and 20 per cent acetic anhydride, it was found that neither the "colour part" nor the "silicate part" is affected. This behaviour is very different from that of thiosulphate and polysulphide, and seems to the author to be analogous to the behaviour of compounds of sulphur with anhydrides, of which as yet only Weber's blue sesquioxide S_2O_3 is known.

New Reagent for Nickel.—L. Tschugaeff. —The most sensitive test for nickel is the brown colouration produced by alkali thiocarbonates, but this reaction is considerably affected by the presence of cobalt. The author has found that α -dimethylglyoxime, $\text{CH}_3\text{C}(\text{N.OH})\text{C}(\text{N.OH})\text{CH}_3$, is an exceedingly sensitive and characteristic reagent for nickel. The solution to be tested is freed from excess of acid by the addition of alkali (preferably ammonia or sodium acetate solution), the powdered dioxime is added, and the solution boiled for a short time. A scarlet precipitate of the composition NiD.DH_2 (DH_2 = dioxime) is produced. If the nickel is present only in very small quantity a yellowish solution is first obtained, from which the red compound separates out on cooling. By this test it is quite easy to demonstrate the presence of nickel in solutions containing only 1 part of nickel in 400,000 parts of water. The reaction is not in the least influenced by the presence of about ten times the quantity of cobalt. But as the cobalt salts form brown compounds with α -dimethyl glyoxime, if larger quantities of cobalt are present it is better to proceed as follows:—A large excess of ammonia is added to the solution to be tested, which is then thoroughly shaken up. Any cobalt salts present are thus converted into the cobalt ammonia compounds. Excess of dioxime is then added, and the solution boiled for a short time. When larger quantities of nickel are present (e.g., in commercial cobalt salts) a scarlet scum forms on the walls of the test-tube, but it is generally necessary to cool, filter, and wash the residue with water. If nickel is present it appears pink, colourless if nickel is absent. In this way 0.1 m.grm. of nickel can be detected in 500 m.grms. of cobalt. Dimethyl glyoxime can now be obtained commercially.

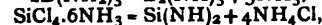
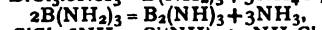
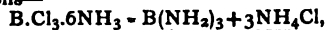
Oxidation of the Nitrogen of the Air by means of the Electric Arc.—F. v. Lepel. —The author uses electrodes which rotate in opposite directions, the anode

consisting of oxidised copper-wire and the cathode of pyrolusite. The colour of the flame is pale greenish yellow or greenish white. The furnace must be wide and roomy, for narrow tubes give smaller yields, and, moreover, favour cooling. A very large absorption chamber, into which water vapour and warm water are introduced, is necessary, and the air must be passed into the furnace obliquely at the rate of about 180 litres an hour. Carbon cathodes are found to be superior to those of pyrolusite. Increasing the length of the flame increases the yield.

Formaldehyde and the Production of Formates.—Hans and Astrid Euler. —Formaldehyde is a feeble acid forming salts with strong bases. A normal solution of formaldehyde mono-sodium salt contains about half the salt as such, while half is split up into free base and free formaldehyde. In dilute solution the formaldehyde salts behave like binary electrolytes; the dissociation constant of the aldehyde as acid amounts to roughly $1 \cdot 10^{-14}$ at 0° . The formation of sodium or barium formate from formaldehyde and sodium or barium hydroxide is a reaction of the second order. If the formaldehyde is present in great excess (thus if its concentration is practically constant), the reaction is of the first order. The value of the constant decreases slightly with the time. The behaviour of caustic soda is very similar to that of barium hydroxide, and the reaction constants are nearly the same, decreasing somewhat as the initial concentration of the formaldehyde rises, on account of the formation of formaldehyde salts. The production of formate is simply a decomposition process, and not an oxidation, for the reaction occurs as quickly in an atmosphere of hydrogen as in an atmosphere of oxygen. Formate is produced much more quickly with lime than with sodium or barium hydroxide. Even if no sugar is formed the dissolved bases possess a specific power of producing formate, and the power of different bases of condensing formaldehyde to sugar is not directly connected with the rate of producing formate.

Effect of Silver Nitrate upon the Solubility of Silver Nitrite.—R. Abegg and H. Pick. —The authors find that the solubility relations of silver nitrite are simply and accurately expressed by Nernst's theory, and they explain the fact that Naumann and Rücker have recently obtained different results by supposing that their mistake is due to their assumption that silver nitrate, being a very difficultly soluble salt, may be regarded as being completely split up into its ions. This by no means always holds good for difficultly soluble salts. While neutral salts are often completely dissociated at a concentration of 0.1 molecule per litre, there are also salts which, at the saturation concentration of only 0.0001, form practically no ions, e.g., HgI_2 .

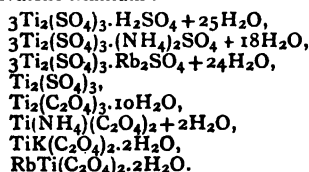
Zirconium Halogen Compounds.—Arthur Stähler and Bruno Denk. —The authors have prepared addition products of zirconium chloride, iodide, and bromide with ammonia, viz., $\text{ZrCl}_4 \cdot 8\text{NH}_3$, $\text{ZrI}_4 \cdot 8\text{NH}_3$, $\text{ZrBr}_4 \cdot 10\text{NH}_3$. The formation of these addition products may be regarded as analogous to the process of taking up water of crystallisation by the so-called complex salts. The similar compounds of boron and silicon, i.e., $\text{BCl}_3 \cdot 6\text{NH}_3$ and $\text{SiCl}_4 \cdot 6\text{NH}_3$, have been shown to be actually mixtures of amide or imide and ammonium chloride, as represented by the equations—



and the zirconium halogen ammonia compounds belong to the same category, as shown by their behaviour towards liquid ammonia. For by washing the iodide compound with liquid ammonia, ammonium iodide can be extracted, and the percentage of zirconium rises from 12 to 45 per cent. The authors have prepared a compound of zirconium iodide and 6 molecules of ethylamine. With ether, ZrI_4 forms yellow, very unstable crystals, which dissolve on addition of excess of ether. These crystals have apparently the composition expressed by the formula

ZrI₄·4(C₂H₅)₂O, but on account of their instability the analytical results cannot be regarded as very trustworthy.

Titanium.—Arthur Stähler and Heinz Wirthwein.—The authors prepare pure titanium material as follows:—The minerals rutile, titanium iron ore, or yttrotitanite, are mixed with carbon and fused in the electric furnace, when carbides are formed. These are then treated with dry chlorine, and the titanium tetrachloride can be separated by distillation. In order to obtain it free from vanadium it is shaken for forty-eight hours with a little sodium amalgam till it becomes quite colourless. When rutile is treated directly with sulphur chloride the iron and vanadium escape as chlorides, while nearly pure titanium oxide remains behind; it is, however, slowly converted completely into chloride, which can not be separated from the sulphur chloride by distillation, owing to the close proximity of the boiling-points of the two liquids. The authors find that, contrary to the statements of former investigators, tetravalent titanium is not coloured yellow by pure ether in presence of alcohol. If hydrogen peroxide is present in the ether the reaction occurs; alcohol need not be present. The authors have prepared the following compounds of trivalent titanium:—



When excess of liquid ammonia is allowed to act upon TiCl₄, the compound TiCl₄·8NH₃ is produced as a yellow powder.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following additional information has been received:—

NORTHAMPTON INSTITUTE, St. John Street Road, E.C.—Principal, R. Mullineux Walmsley, D.Sc., F.R.S.E.—This Institute is a Technical, Social, and Recreative Institute for both sexes. It was founded as a branch of the City Polytechnic, and its educational aim is to provide classes in technological and trade subjects. The educational courses fall into two distinct sections:—(a) Day Courses for students who are willing to give the whole of their time for one or more years to a thorough systematic training in one of the technological subjects dealt with; and (b) Evening Courses and Classes for those who are unable to attend during the daytime. Day and Evening Courses in Engineering (Mechanical and Electrical), Technical Optics, in Artistic Crafts, and Horology (commencing Monday, October 2). Evening Courses in Technical Chemistry and Domestic Economy (commencing Monday, September 25).

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Established in 1710 as a Foundation School by the generosity of the citizen whose name it bears, after several developments, and as a result of increased revenues, it has now become a popular educational centre, and one of the Polytechnics aided by the London County Council. The new building was formally opened in 1902, and the fourth session will begin on Monday next, the 25th inst. Thoroughly complete laboratories and workshops are provided for instruction in Metallurgy, Assaying, Metal work, Jewellery, Enamelling, Glass-blowing, &c., under an efficient teaching staff, and courses of study are arranged for those engaged in chemical and electrical industries. Classes are also held in other branches of education.

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Appointment.—Mr. E. Towyn Jones, B.Sc., Demonstrator in Chemistry at University College, Bangor, has been appointed Assistant-Lecturer and Senior Demonstrator in the Department of Chemistry and Physics of the Pharmaceutical Society of Great Britain.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Pine Tar.—Can any reader give reliable information respecting the commercial value of pine tar on English markets? Also in what industry or industries the product is used.—W. E. L.

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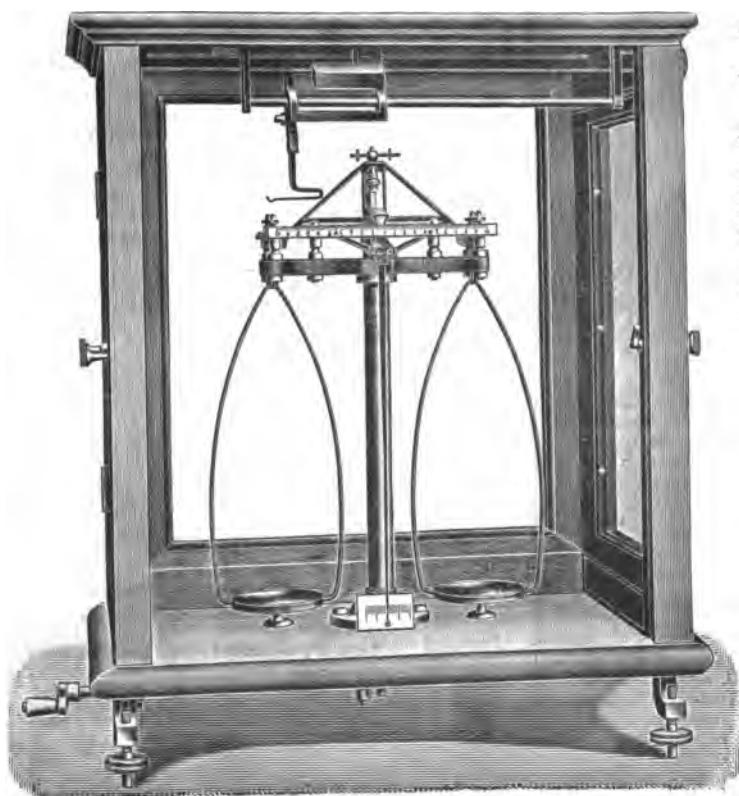
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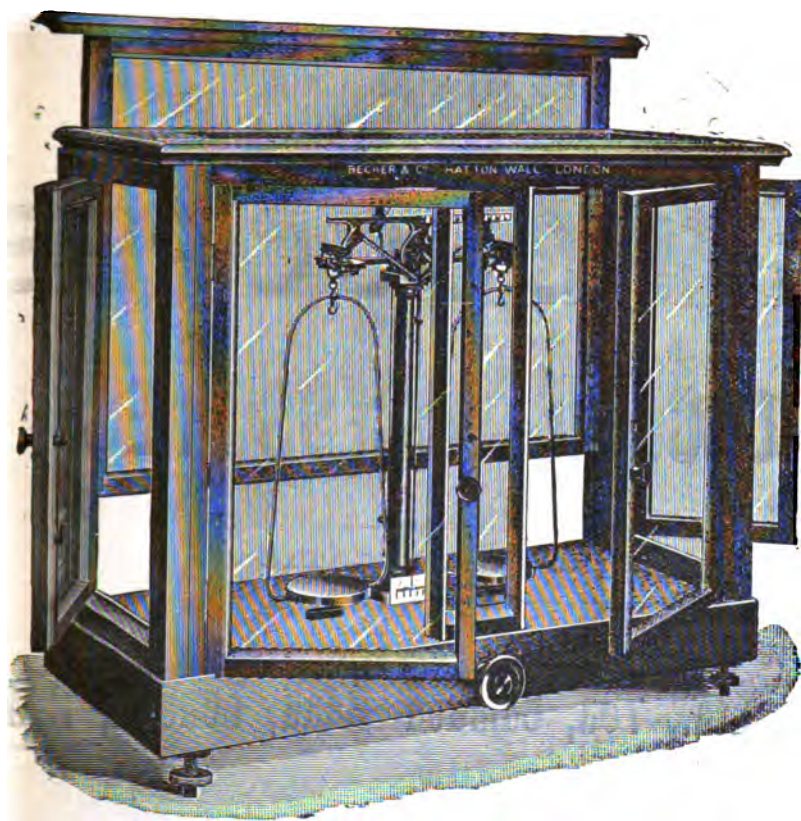
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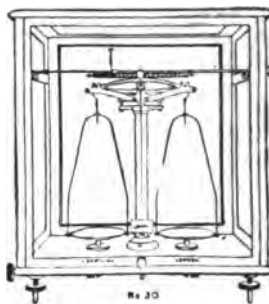
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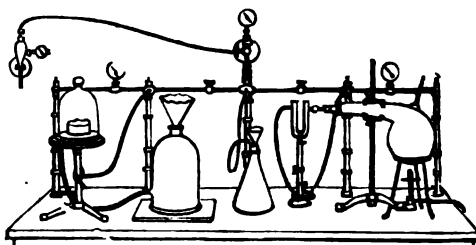
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THE CHEMICAL NEWS.

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DIAMONDS.

A LECTURE DELIVERED BEFORE THE BRITISH ASSOCIATION
AT KIMBERLEY, SEPTEMBER 5, 1905.

By Sir WILLIAM CROOKES,
Hon. D.Sc. (Oxford and Dublin), F.R.S.

(Continued from p. 140).

Genesis of the Diamond.

SPECULATIONS as to the probable origin of the diamond have been greatly forwarded by patient research, and particularly by improved means of obtaining high temperatures, an advance we owe principally to the researches of Professor Moissan.

Until recent years carbon was considered absolutely non-volatile and infusible; but the enormous temperatures at the disposal of experimentalists—by the introduction of electricity—show that, instead of breaking rules, carbon obeys the same laws that govern other bodies. It volatilises at the ordinary pressure at a temperature of about $3600^{\circ}\text{C}.$, and passes from the solid to the gaseous state without liquefying. It has been found that other bodies, such as arsenic, which volatilises without liquefying at the ordinary pressure, will easily liquefy if pressure is added to temperature. It naturally follows that if along with the requisite temperature sufficient pressure is applied, liquefaction of carbon will take place, when on cooling it will crystallise, but carbon at high temperatures is a most energetic chemical agent, and if it can get hold of oxygen from the atmosphere or any compound containing it, it will oxidise and fly off in the form of carbonic acid. Heat and pressure therefore are of no avail unless the carbon can be kept inert.

It has long been known that iron when melted dissolves carbon, and on cooling liberates it in the form of graphite. Moissan discovered that several other metals, especially silver, have similar properties; but iron is the best solvent for carbon. The quantity of carbon entering into solution increases with the temperature.

For the manufacture of—I am afraid I must say an infinitesimal—diamond, the first necessity is to select pure iron—free from sulphur, silicon, phosphorus, &c.,—and to pack it in a carbon crucible with pure charcoal from sugar. The crucible is then put into the body of the electric furnace, and a powerful arc formed close above it between carbon poles, utilising a current of 700 ampères at 40 volts pressure. The iron rapidly melts and saturates itself with carbon. After a few minutes heating to a temperature above $4000^{\circ}\text{C}.$ —a temperature at which the iron melts like wax and volatilises in clouds—the current is stopped, and the dazzling fiery crucible is plunged beneath the surface of cold water, where it is held until it sinks below a red heat. As is well known, iron increases in volume at the moment of passing from the liquid to the solid state. The sudden cooling solidifies the outer layer of iron and holds the inner molten mass in a tight grip. The expansion of the inner liquid on solidifying produces an enormous pressure, and under the stress of this pressure the dissolved carbon separates out in transparent forms—minutely microscopic, it is true—all the same veritable diamonds, with crystalline form and appearance, colour, hardness, and action on light the same as the natural gem.

Now commences the tedious part of the process. The metallic ingot is attacked with hot nitro-hydrochloric acid until no more iron is dissolved. The bulky residue consists chiefly of graphite, together with translucent chestnut-coloured flakes of carbon, black opaque carbon of a density of from 3.0 to 3.5, and hard as diamonds—black diamonds

or carbonado, in fact,—and a small portion of transparent colourless diamonds showing crystalline structure. Besides these, there may be carbide of silicon and corundum, arising from impurities in the materials employed.

The residue is first heated for some hours with strong sulphuric acid at the boiling point, with the cautious addition of powdered nitre. It is then well washed, and for two days allowed to soak in strong hydrofluoric acid in cold, then in boiling acid. After this treatment the soft graphite disappears, and most if not all the silicon compounds have been destroyed. Hot sulphuric acid is again applied to destroy the fluorides, and the residue, well washed, is attacked with a mixture of the strongest nitric acid and powdered potassium chlorate, kept warm—but not above $60^{\circ}\text{C}.$, to avoid explosions. This treatment must be repeated six or eight times, when all the hard graphite will gradually be dissolved, and little else left but graphitic oxide, diamond, and the harder carbonado and boart. The residue is fused for an hour in fluorhydrate of fluoride of potassium, then boiled out in water, and again heated in sulphuric acid. The well washed grains which resist this energetic treatment are dried, carefully deposited on a slide, and examined under the microscope. Along with numerous pieces of black diamond are seen transparent colourless pieces, some amorphous, others with a crystalline appearance. Although many fragments of crystals occur, it is remarkable I have never seen a complete crystal. All appear shattered, as if on being liberated from the intense pressure under which they were formed they burst asunder. I have singular evidence of this phenomenon. A fine piece of artificial diamond, carefully mounted by me on a microscopic slide, exploded during the night and covered the slide with fragments. Moissan's crystals of artificial diamond sometimes broke a few weeks after their preparation, and some of the diamonds which cracked weeks or even months after their preparation showed fissures covered with minute cubes. This bursting paroxysm is not unknown at the Kimberley mines.

On the screen I will project photographs of artificial diamonds manufactured in the manner described. So far, these specimens are all microscopic. The largest artificial diamond is less than one millimetre across.

These laboratory diamonds burn in the air before the blowpipe to carbonic acid. In lustre, crystalline form, optical properties, density, and hardness, they are identical with the natural stone.

In several cases Moissan separated ten to fifteen microscopic diamonds from a single ingot. The larger of these are about 0.75 m.m. long; the octahedra being 0.2 m.m.

Graphite.

Intermediate between soft carbon and diamond come the graphites. The name graphite is given to a variety of carbon, generally crystalline, which in an oxidising mixture of chlorate of potassium and nitric acid forms graphitic oxide. This varies in colour from green to brown or yellow, or it is almost without colour, according to the completeness of the reaction. Graphites are of varying densities, from 2.0 to 3.0, and generally of crystalline aspect. Graphite and diamond pass insensibly into one another. Hard graphite and soft diamond are near the same specific gravity. The difference appears to be one of pressure at the time of formation.

Some forms of graphite exhibit the remarkable property by which it is possible to ascertain approximately the temperature at which they were formed, or to which they have subsequently been exposed. Sprouting graphite is a form, frequently met with in nature, which on moderate heating swells up to a bulky, very light mass of amorphous carbon. Moissan has found it in blue ground from Kimberley; my own results verify his. When obtained by simple elevation of temperature in the arc or the electric furnace graphites do not sprout; but when they are formed by dissolving carbon in a metal at a high temperature and then allowing the graphite to separate out on cooling, the sprouting variety appears. The phenomenon of sprouting is easily

shown. I place a few grains in a test-tube and heat it to about 170° C., when you see the grains increase enormously in bulk and fill the tube with a light form of amorphous carbon.

The resistance of a graphite to oxidising agents is greater the higher the temperature to which it has previously been exposed. Graphites which are easily attacked by a mixture of fuming nitric acid and potassium chlorate are rendered more resistant by strong heat in the electric furnace.

Boiling- and Melting-point of Carbon.

On the average the critical-point of a substance is 1.5 times its absolute boiling-point. Therefore the critical-point of carbon should be about 5800° Ab. But the absolute critical temperature divided by the critical pressure is for all the elements so far examined never less than 2.5; this being about the value Sir James Dewar finds for hydrogen. So that, accepting this, we get the maximum critical pressure as follows, viz., 2320 atmospheres:—

$$\frac{5800^\circ \text{ Ab.}}{\text{CrP}} = 2.5, \text{ or } \text{CrP} = \frac{5800^\circ \text{ Ab.}}{2.5}, \text{ or } 2320 \text{ atmospheres.}$$

Carbon and arsenic are the only two elements that have a melting-point above the boiling-point; and among compounds carbonic acid and fluoride of silicon are the only other bodies with similar properties. Now the melting-point of arsenic is about 1.2 times its absolute boiling-point. With carbonic acid and fluoride of silicon the melting-points are about 1.1 times their boiling-points. Applying these ratios to carbon we find that its melting-point would be about 4400°.

Therefore, assuming the following data

Boiling-point	3870° Ab.
Melting-point	4400
Critical temperature ..	5800
Critical pressure	2320 Ats.

the Rankine or Van der Waals formula calculated from the boiling-point and critical data would be as follows:—

$$\log P = 10.11 - 39120/T,$$

and this gives for a temperature of 4400° Ab. a pressure of 16.6 Ats. as the melting-point pressure. The results of the formula are given in the form of a table:—

Temperature.	Pressure.	
Ab.	Ats.	
3870°	1.00	Boiling-point.
4000	2.14	
4200	6.25	
4400	16.6	Melting-point.
4600	40.4	
4800	91.2	
5000	193	
5200	386	
5400	735	
5600	1330	
5800	2320	Critical-point (15 tons per square inch).

If then we may reason from these rough estimates, above a temperature of 5800° Ab. no amount of pressure will cause carbon vapour to assume liquid form, whilst at 4400° Ab. a pressure of above 17 atmospheres would suffice to liquefy some of it. Between these extremes the curve of vapour pressure is assumed to be logarithmic, as represented in the accompanying diagram. The constant 39120 which occurs in the logarithmic formula enables us to calculate the latent heat of evaporation. If we assume the vapour density to be normal, or the molecule in vapour as C₂, then the heat of volatilisation of 12 grms. of carbon would be 90,000 calories; or, if the vapour is a condensed molecule like C₆, then the 12 grms. would need 30,000 calories. In the latter case the evaporation of 1 grm. of carbon would require 2500 calories, whereas a substance like zinc needs only about 400 calories.

A New Formation of Diamond.

I have long speculated as to the possibility of obtaining artificially such pressures and temperatures as would fulfil the above conditions. In their researches on the gases from fired gunpowder and cordite, Sir Frederick Abel and Sir Andrew Noble obtained in closed steel cylinders pressures as great as 95 tons to the square inch, and temperatures as high as 4000° C. According to a paper recently communicated to the Royal Society, Sir Andrew Noble, exploding cordite in closed vessels, has obtained a pressure of 8000 atmospheres, or 50 tons per square inch, with a temperature reaching in all probability 5400° Ab.

Here, then, we have conditions favourable for the liquefaction of carbon, and were the time of explosion sufficient to allow the reactions to take place, we should certainly expect to get the liquid carbon to solidify in the crystalline state.*

By the kindness of Sir Andrew Noble I have been enabled to work upon some of the residues obtained in closed vessels after explosions, and I have submitted them to the same treatment that the granulated iron had gone through. After weeks of patient toil I removed the amorphous carbon, the graphite, the silica,† and other constituents of the ash of cordite, and obtained a residue among which, under the microscope, crystalline particles could be distinguished. Some of these particles, from their crystalline appearance and double refraction, were silicon carbide; others were probably diamonds. The whole residue was dried and fused at a good red heat in an excess of potassium bifuoride, to which was added during fusion 5 per cent of nitre. (Previous experiments had shown me that this mixture readily attacked and dissolved silicon carbide; unfortunately it also attacks diamond to a slight degree). The residue, after thorough washing and then heating in fuming sulphuric acid, was washed, dried, and the largest crystalline particles picked out and mounted. All the operations of washing and acid treatment were performed in a large platinum crucible by decantation (except the preliminary attack with nitric acid and potassium chlorate, when a hard glass vessel was used); the final result was washed into a shallow watch-glass and the selection made under the microscope.

I project on the screen a few photographs of these crystals. From the treatment they have undergone, chemists will agree with me that diamonds only could stand such an ordeal; on submitting them to skilled crystallographic authorities my opinion is confirmed. Speaking of the one before you (303), Professor Bonney calls it "a diamond showing octahedral planes with dark boundaries due to high refracting index." After careful examination, Professor Miers writes of the same crystal diamond:—"I think one may safely say that the position and angles of its faces, and of its cleavages, the absence of birefringence, and the high refractive index, are all compatible with the properties of the diamond crystallising in the form of an octahedron. Others of the remaining crystals, which show a similar high refractive index, appeared to me to present the same features."

It would have been more conclusive had I been able to get further evidence as to the density and hardness of the crystals; but I am still working at the subject, and hope to add these confirmatory tests. From what I have already said I think there is no doubt that in these closed vessel

* Sir James Dewar, in a Friday Evening Discourse at the Royal Institution, 1880, showed an experiment proving that the temperature of the interior of a carbon tube heated by an outside electric arc was higher than that of the oxy-hydrogen flame. He placed a few small crystals of diamond in the carbon tube, and, maintaining a current of hydrogen to prevent oxidation, raised the temperature of the tube in an electric furnace to that of the arc. In a few minutes the diamond was transformed into graphite. At first sight this would seem to show that diamond cannot be formed at temperatures above that of the arc. It is probable, however, for reasons given above, that at exceedingly high pressures the result would be different.

† The silica was in the form of spheres, perfectly shaped and transparent, mostly colourless, but among them several of a ruby colour. When 5 per cent of silica was added to cordite, the residue of the closed vessel explosion contained a much larger quantity of these spheres.

explosions we have another method of producing the diamond artificially.

Sensational as is the story of the diamond industry in South Africa, quite another aspect fixes the attention of the chemist. The diamonds come out of the mines, but how did they get in? How were they formed? What is their origin?

Gardner Williams, who knows more about diamonds than any man living, is little inclined to indulge in specula-

which would be based on any non-assailable data.' All that can be said is that in some unknown manner carbon, which existed deep down in the internal regions of the earth, was changed from its black and uninviting appearance to the most beautiful gem which ever saw the light of day."

Meteoritic Diamonds.

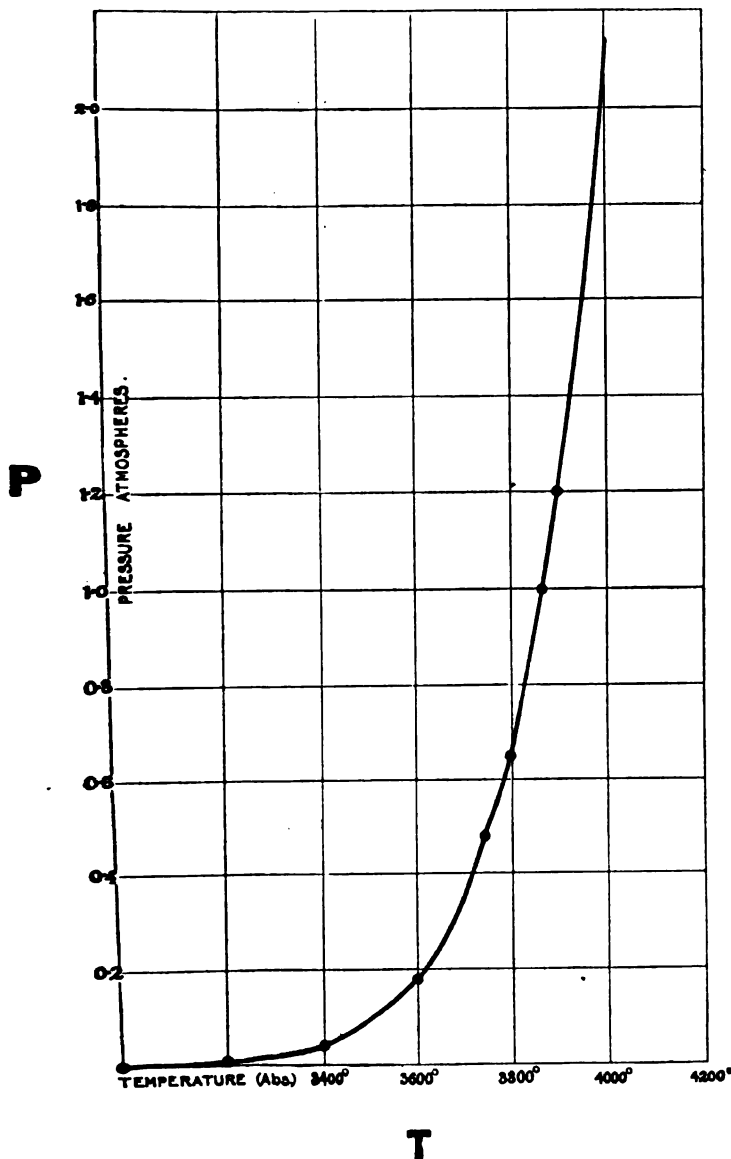
Another diamond theory appeals to the fancy. It is said the diamond is a gift from Heaven, conveyed to earth in meteoric showers. The suggestion, I believe, was first broached by A. Meydenbauer, who says (CHEMICAL NEWS, 1890, vol. lxi., p. 209):—"The diamond can only be of cosmic origin, having fallen as a meteorite at later periods of the earth's formation. The available localities of the diamond contain the residues of not very compact meteoric masses which may, perhaps, have fallen in prehistoric ages, and which have penetrated more or less deeply, according to the more or less resistant character of the surface where they fell. Their remains are crumbling away on exposure to the air and sun, and the rain has long ago washed away all prominent masses. The enclosed diamonds have remained scattered in the river beds, while the fine light matrix has been swept away."

According to this hypothesis, the so-called volcanic pipes are simply holes bored in the solid earth by the impact of monstrous meteors—the larger masses boring the holes, while the smaller masses, disintegrating in their fall, distributed diamonds broadcast. Bizarre as such a theory appears, I am bound to say there are many circumstances which show that the notion of the Heavens raining diamonds is not impossible.

The most striking confirmation of the meteoric theory comes from Arizona. Here, on a broad open plain, over an area about five miles in diameter, have been scattered one or two thousand masses of metallic iron, the fragments varying in weight from half a ton to a fraction of an ounce. There is little doubt these masses formed part of a meteoric shower, although no record exists as to when the fall took place. Curiously enough, near the centre, where most of the meteorites have been found, is a crater with raised edges three-quarters of a mile in diameter and about 600 feet deep, bearing exactly the appearance which would be produced had a mighty mass of iron struck the ground and buried itself deep under the surface. Altogether ten tons of this iron have been collected, and specimens of the Canyon Diablo meteorite are in most collectors' cabinets.

An ardent mineralogist—the late Dr. Foote—cutting a section of this meteorite, found the tools were injured by something vastly harder than metallic iron. He examined the specimen chemically, and soon after announced to the scientific world that the Canyon Diablo meteorite contained black and transparent diamonds. This startling

discovery was afterwards verified by Professors Moissan and Friedel, and Moissan working on 183 kilogrammes of the Canyon Diablo meteorite, has recently found smooth black diamonds and transparent diamonds in the form of octahedra with rounded edges, together with green hexagonal crystals of carbon silicide. The presence of carbon silicide in the meteorite shows that it must, at some time, have experienced the temperature of the electric furnace. Since this revelation, the search for



tion. In his fascinating book he frankly says ("The Diamond Mines of South Africa," p. 510; Macmillans, 1902):—

"I have been frequently asked, 'What is your theory of the original crystallisation of the diamond?' and the answer has always been, 'I have none; for after seventeen years of thoughtful study, coupled with practical research, I find that it is easier to "drive a coach and four" through most theories that have been propounded than to suggest one

diamonds in meteorites has occupied the attention of chemists all over the world.

I am enabled to show you photographs of true diamonds I myself have extracted from the Canyon Diablo meteorite. A fine slab of the meteorite, weighing about seven pounds, is on the table before you.

Here, then, we have incontestable proof of the truth of the meteoric theory. Under atmospheric influences the iron would rapidly oxidise and rust away, colouring the adjacent soil with red oxide of iron. The meteoric diamonds would be unaffected, and left on the surface of the soil, to be found haphazard when oxidation had removed the last proof of their celestial origin. That there are still lumps of iron left at Arizona is merely due to the extreme dryness of the climate and the comparatively short time that the iron has been on our planet. We are here witnesses to the course of an event which may have happened in geologic times anywhere on the earth's surface.

Although in Arizona diamonds have fallen from the skies, confounding our senses, this descent of precious stones is what may be called a freak of Nature rather than a normal occurrence. To the modern student of science there is no great difference between the composition of our earth and that of extra-terrestrial masses. The mineral periodot is a constant extra-terrestrial visitor, present in most meteorites. And yet no one doubts that periodot is also a true constituent of rocks formed on this earth. The spectroscope reveals that the elementary composition of the stars and the earth are pretty much the same; and the spectroscope also shows that meteorites have as much of earth as of heaven in their composition. Indeed, not only are the selfsame elements present in meteorites, but they are combined in the same way to form the same minerals as in the crust of the earth.

It is certain from observations I have made, corroborated by experience gained in the laboratory, that iron at a high temperature and under great pressure—conditions existent at great depths below the surface of the earth—acts as the long-sought solvent for carbon, and will allow it to crystallise out in the form of diamond. But it is also certain, from the evidence afforded by the Arizona and other meteorites, that similar conditions have existed among bodies in space, and that on more than one occasion a meteorite freighted with jewels has fallen as a star from the sky.

Many circumstances point to the conclusion that the diamond of the chemist and the diamond of the mine are strangely akin as to origin. It is evident that the diamond has not been formed *in situ* in the blue ground. The genesis must have taken place at vast depths under enormous pressure. The explosion of large diamonds on coming to the surface shows extreme tension. More diamonds are found in fragments and splinters than in perfect crystals; and it is noteworthy that although these splinters and fragments must be derived from the breaking up of a large crystal, yet in only one instance have pieces been found which could be fitted together, and these occurred at different levels. Does not this fact point to the conclusion that the blue ground is not their true matrix? Nature does not make fragments of crystals. As the edges of the crystals are still sharp and unabraded, the *locus* of formation cannot have been very distant from the present sites. There were probably many sites of crystallisation differing in place and time, or we should not see such distinctive characters in the gems from different mines, nor indeed in the diamonds from different parts of the same mine.

It is not difficult to imagine that masses of iron saturated with carbon existed formerly at a sufficient depth below the present mines, where temperature and pressure would produce the reactions which laboratory experiments show to be probable.

(To be continued).

Morphine may be used for detecting formaldehyde, and, inversely, formaldehyde detects morphine and its derivatives. —*Chemist and Druggist*.

THE RATE OF OXIDATION IN GASEOUS OXYGEN.

By W. P. JORISSEN and W. E. RINGER.

1. As is well known, the hypothesis of van't Hoff (*Zeit. f. Phys. Chem.*, 1895, xvi., 411; see also Ewan's translation of van't Hoff-Cohen's "Studien zur Chemischen Dynamik," 1896) concerning the activation of oxygen stands in connection with the results of Ewan's experiments on the rate of oxidation in dried oxygen (see also Jorissen, *Zeit. f. Phys. Chem.*, 1897, xxii., 34, 47; 1897, xxiii., 667; *Ber.*, 1896, xxix., 1707; 1897, xxx., 1952; *Arch. Néerl.*, 1897, viz., the proportionality of this rate with the square root of the pressure of the oxygen (*Phil. Mag.*, 1894, [5], xxxviii., 512; *Zeit. f. Phys. Chem.*, 1895, xvi., 317). This hypothesis, however, was somewhat obscured by that of Bach (*Monit. Scientif.*, July, 1897; J. W. Mellor, "Chem. Statics and Dynamics," 1904, 314) and Engler (Engler and Wild, *Ber.*, 1897, xxx., 1674; Engler and Weissberg, "Kritische Studien über die Vorgänge der Autoxydation," 1904).

Several phenomena, however, which accompany the oxidation of phosphorus have again brought it forward, though in a somewhat changed shape. (See paper by W. P. Jorissen, *CHEMICAL NEWS*, xcii., 62).

In connection with this revival, the controlling of the result obtained by Ewan is desirable. For this it will be best to study the case of a homogeneous mixture of oxygen and a gaseous spontaneously oxidising substance (autoxidiser), the product of oxidation being also gaseous. The oxidation of acetaldehyde, studied by Ewan, nearly represents this case, but the acetic acid which is formed soon condenses and then acts as a solvent for the aldehyde, thus giving rise to a complication.

If the autoxidiser is a liquid (for instance, benzaldehyde, Jorissen, *Chem. Weekblad.*, 1904, i., 803) or a solid (phosphorus and sulphur, Ewan, *loc. cit.*) the influence of the rate of evaporation and of diffusion comes forward.

Nernst and Brunner have drawn the attention to the fact that, in many cases of heterogeneous reactions, the velocity which is measured is only a velocity of diffusion and not the velocity of the reaction (*Zeit. f. Phys. Chem.*, 1904, xlvii., 52, 55; see also J. W. Mellor, "Chem. Statics and Dynamics," 1904, 125–140).

Ewan took the influence of the rate of evaporation of the autoxidiser into account, and supposes that the oxidation takes place in the very neighbourhood of the autoxidiser if the pressure of the oxygen is not too small.

But the question remains: is the rate of oxidation greater or smaller than the rate of evaporation? And this rate of evaporation depends again on the size and nature of the surface of the substance.

A very interesting phenomenon in the dominion of the oxidation processes is the so-called "boundary-pressure" (see *f.i.* Mellor, *loc. cit.*, pp. 417–428, 440–443). This pressure has been studied best for the oxidation of phosphorus (Joubert, Ewan, Centnerazwer, E. J. Russell). Joubert found indications for this limit in the case of sulphur and arsenic (Thèses, 1874, 16–17). Ewan also has presumptions as regards sulphur, and his experiments made the existence of a limiting-pressure in the case of acetaldehyde probable.

It remains to be said that the rate of oxidation of a few substances (see Mellor, *loc. cit.*, p. 442), for instance, phosphine (Houton de Labillardière, van't Hoff, "Etudes," 1884, 60–67; Van de Stadt, *Zeit. f. Phys. Chem.*, 1893, xii., 322), is accelerated by diminishing the pressure. In very few cases only the existence of a boundary-pressure has been investigated. In the case of nickel carbonyl the spontaneous inflammability was still observed at a pressure of 13 atmospheres (Reicher and Jorissen, *Maandbl. v. Natuurwetensch.*, 1894, No. 1), while the oxidation of benzaldehyde in not dried oxygen still takes place in the dark at a pressure of 8.2 atmospheres (Jorissen, *Chem. Weekblad.*, 1904, i., 805).

2. The method, used by Joubert (Thèses, Paris, 1874) in his experiments on the boundary pressure in the case of phosphorus, consisted in the determination at a given temperature of the pressure at which the glow appeared. He made use of pure oxygen (does not speak, however, of drying this gas), and let it enter into the evacuated apparatus, which was connected with an open mercury manometer as described by Regnault. After making his eyes sensitive by remaining in the dark for some time, he let the mercury flow out till the glow became perceptible. Then he increased the pressure till the glow disappeared, let the mercury flow out again, &c. The average of six observations (at one and the same temperature), which differed 10 to 15 m.m., he accepted as the boundary-pressure. The experiments made at the same temperature with oxygen and phosphorus of different preparations gave large differences between them. Thus he found, for instance, in two series:—

11°5'	580 m.m.	11°0'	495 m.m.
14°2'	650 "	15°2'	570 "
18°0'	730 "	16°0'	595 "
19°2'	760 "		

He confesses that he does not feel sure to what cause he must ascribe this, and does not seem to have considered the possible influence of moisture.

Ewan (*loc. cit.*), who traced the oxidation of phosphorus by looking for a change of the manometer at a given pressure and temperature, mentions that in wet oxygen at a temperature of 20°4' to 20°7' no oxidation was to be observed at a pressure of 695·6 m.m. in twenty-two minutes; it was observed, however, after fifty minutes. At a temperature of 20°43' to 20°64' no oxidation took place at a pressure of 722·8 m.m. in fifty-two minutes, while it became perceptible at a pressure of 671·1 m.m. in forty-three minutes.

In using oxygen dried by means of phosphorus pentoxide at a temperature of 20°87' to 21°26' no oxidation was observed at a pressure of 377·0 m.m. (after seventy minutes), while again perceptible at a pressure of 201·6 m.m. (after one hundred and ten minutes).

Centnerszwer mentions as the boundary pressure in wet oxygen at 20° 567 m.m. (*Zeit. f. Phys. Chem.*, 1898, xxvi., 21). Just like Joubert, he observed the pressure at which the phosphorus began to become luminous while diminishing the pressure by means of an air-pump. The more slowly he evacuated the higher the pressure was found to be at which a glowing was perceptible. The observations, however, gave differences of 50 m.m. As a rule, the diminishing of the pressure till this point was reached, took forty-five to sixty minutes, and in this way he made observations which agreed sufficiently well with each other. As, however, he describes an intermittent phosphorescence which took place at a pressure 50 m.m. above the glow pressure, the latter must be much lower than the real boundary pressure.

E. J. Russell (*Journ. Chem. Soc.*, December, 1903, p. 1279) did not observe an oxidation of phosphorus in wet oxygen under high pressures even after six months; however, he did not find a boundary pressure in oxygen dried by sulphuric acid.

As Ewan observed such a pressure in oxygen dried by phosphorus pentoxide, and Brereton Baker* could not observe an oxidation of phosphorus at all in oxygen dried for a long time by this substance, this behaviour of sulphuric acid as a drying agent would appear strange.

Now, Russell let the oxygen, prepared by heating pure chlorate or permanganate of potassium, enter the apparatus, in which the phosphorus was present, without taking care to exclude possible traces of ozone† or oxygen ions.

Therefore when undertaking to study the boundary pressure of oxygen, we came to the conclusion that it would be necessary to prepare the oxygen beforehand, and only to use it after waiting for some days, washing it by means of solutions of potassium iodide and caustic potash, and drying it by chloride of calcium.

We also chose as a method of observation that of Ewan, viz., the manometric, and used as a liquid for the manometer either water or water-free glycerin.

The apparatus consisted in a vessel of about 100 c.m.³, provided with a supply tube with tap, so that oxygen could be passed through. The vessel was closed by a ground hollow stopper, to which a thin test-tube was soldered. This test-tube was covered by a layer of pure phosphorus, which could be kept cold by a stream of water flowing through the tube, and of the same temperature (15°) as the water which filled the thermostat. In this thermostat, which was kept at a constant temperature by means of a toluol regulator, the vessel and a flask, which will be described presently, were immersed. To the vessel was also soldered a tube which led to a manometer with water or glycerin, and also to the above-mentioned flask. This flask, partly filled with mercury, was closed by a cork soaked with paraffin and covered with sealing-wax, through which passed four tubes. One of these tubes connected the flask with the vessel, the second with a mercury manometer, the third with a mercury syphon which enabled us to increase or to decrease the pressure in the flask (and the vessel) slowly or quickly. The fourth tube served as a gas abduction tube, and was provided with a tap. The results are briefly communicated below.

Oxygen* Saturated with Water-vapour, Temperature 15° C.

Experiment 1.—No oxidation perceptible at a pressure of 633 m.m. (twenty minutes), which was, however, to be observed at 604 m.m. (32 m.m. of water in sixteen minutes).

Experiment 2.—No oxidation at a pressure of 628 m.m. (seventeen minutes), oxidation at 598 m.m. (27 m.m. of water in forty minutes).

At Experiment 2 a retardation was observed at the beginning. Even at a pressure of 525 m.m. no oxidation took place (seven minutes); it did, however, take place at 508 m.m. (33 m.m. of water in seven minutes). On our increasing the pressure to 628 m.m. the oxidation stopped.

At Experiment 1, where the oxidation took place at a pressure of 604 m.m., we increased the pressure after sixteen minutes to 623 m.m. The oxidation, however, did not stop; after eight minutes the pressure was increased to 634 m.m.—still the oxidation went on. After eighteen minutes, the pressure being increased to 648 m.m., the same took place; also when after thirty-four minutes the pressure was brought as high as 680 m.m. At this pressure, however, the oxidation went on very slowly (8 m.m. of water in twenty-nine minutes). The layer of phosphorus was not the same in Experiments 1 and 2.

With the layer of Experiment 1 a large number of experiments were made. Between each series of experiments the phosphorus was kept in the dark submersed in water.

During these observations some c.c. of a 10 per cent solution of potassium iodide were present in the vessel in order to absorb the ozone which might be formed.

The following retardations were now observed:—

a.	No oxidation at 520 m.m. (25 minutes), but at 512 m.m.
b.	" 592 " (34 "), " 527 "
c.	" 525 " (26 "), " 476 "
d.	" 513 " (10 "), " 495 "
e.	" 514 " (10 "), neither at 481·5 m.m. (5 minutes), but at 464 m.m.

The oxidation having once begun, the pressure was

* The oxygen contained in Experiment 1 4·3 per cent, in Experiment 2 4·2 per cent of nitrogen, determined after having made the oxygen pass through the apparatus for a long time. The pressure of the oxygen was corrected by means of the result of this analysis. According to Centnerszwer 5 per cent of nitrogen would lower the boundary pressure with 13 m.m.

* *Phil Trans.*, 1888, 571. He says:—"The pressure was varied in every possible way," but it does not seem to be sure that he experimented at very low pressures.

† For the influence of traces of ozone see Chappuis, *Bull. Soc. Chim. de Paris*, 1881, xxxv., 419.

quickly increased to about 633 m.m., at which pressure the oxidation soon ceased. After that the pressure was again lowered. If oxidation took place it was again stopped by increasing the pressure to 633 m.m., &c. As a rule no further retardation was found during such a series of observations.

We were now able to enclose the boundary pressure between two limits* :—

No oxidation.	Oxidation.
626 m.m. (45 mins.)	593 (7 m.m. of water in 22 mins.)
601 " (78 ")	591 (27 " " 80 ")
637 " (39 ")	602 (7.5 " " 26 ")
604 " (40 ")	

The pressures at which oxidation took place in presence of a solution of potassium iodide were practically found to be the same as those observed in the experiments when only water was present.†

In round figures the boundary pressure can be fixed at 600 m.m. at a temperature of 15°.

Oxygen Dried beforehand by means of Calcium Chloride.

—In the vessel, calcium chloride and caustic soda; in the manometer, glycerin was used. At 738 m.m. no oxidation was perceptible in fifteen hours, at 638 and 609 m.m. practically no oxidation either (respectively after three and two hours); at 592 m.m. in fourteen hours a decrease of pressure of about 1.5 m.m. of mercury was observed; at 534 m.m. in six hours a decrease of about 2 m.m. of mercury.

Oxygen Dried beforehand by means of Calcium Chloride.

—In the vessel, sulphuric acid; in the manometer, glycerin was used. In order to dry the phosphorus the drops of water were taken away from its surface by means of blotting-paper, and then it was put for some time in an atmosphere of carbon dioxide, dried by means of calcium chloride. On bringing the phosphorus in the vessel it was for a short time exposed to the ordinary air, and so it was impossible to prevent some oxidation taking place. The rate of this oxidation, which went on in the vessel, could be traced by means of the glycerin manometer, and in that way it was found that the rate decreased gradually. For instance, in the first seventeen minutes the absorption corresponded with 40 m.m. of glycerin, but thereupon in fourteen minutes with 22 m.m. After eighteen hours the rate was only 5 m.m. of glycerin in forty minutes; in the next twenty-four hours the pressure diminished with about 1 m.m. of mercury. After waiting again for forty-eight hours it was observed that during the last twenty hours the pressure had not changed at all.

The pressure of the oxygen at that moment was 725 m.m.‡ On diminishing the pressure to 678 m.m. (eighty minutes), 631 m.m. (fifty-five minutes), 634 m.m. (two hundred and sixty minutes), and 585 m.m. (fifty-five minutes) no oxidation was perceptible at all. When, however, the pressure was decreased to 538 m.m. a very slow oxidation was observed, during which, in seventeen hours, a quantity of oxygen was absorbed corresponding with about 4 m.m. of mercury.

On increasing the pressure again to 728 m.m. the oxidation stopped.

After some days the pressure was lowered to 526 m.m. Again oxidation took place; in sixteen hours a diminution of the pressure of about 6 m.m. of mercury was observed.

Oxygen Dried beforehand by Phosphorus Pentoxide.—In the vessel, phosphorus pentoxide; in the manometer, glycerin was used. Also in this case some oxidation was observed in the beginning of the experiments, but it stopped much sooner than in the case of sulphuric acid being used.

From a large number of experiments, made under these

circumstances, we quote that at 445 m.m. no oxidation was perceptible after eleven hours, and that the highest pressure at which an oxidation could be observed with certainty was 330 m.m. (about 0.5 m.m. of mercury in 175 hours, after that about 1.5 m.m. in 2.5 hours).

These experiments will be repeated with different mixtures of sulphuric acid and water in the vessel; thus in oxygen with water-vapour of different pressures. As to the influence of different radiations, we only state that 5 m.grms. of pure radium bromide (manufactured by Dr. Richard Sthamer, Hamburg) appeared to have no perceptible influence. The oxygen was exposed in this experiment to the influence of this substance in exactly the same way as was the case in our experiments (*Ber.*, 1905, xxxviii., 899) on the influence of radium rays on a mixture of hydrogen and chlorine, which gave a positive result. An influence of the light of an electric arc on the boundary pressure was observed, however. The thermal radiations were kept back as much as possible by means of a small vessel filled with water, while the bundle of light must also penetrate the layer of water in the thermostat.

Whereas the decrease of pressure in the dark was 6.5 m.m. of water in sixty-eight minutes (the pressure thus being very near to the boundary pressure); this decrease amounted to 116 m.m. of water in one hundred and three minutes after the light was put on.

When the light was extinguished it was found to be 60 m.m. of water in forty-eight minutes. The rate of oxidation, therefore, still increased after the light being extinguished.

Of more importance will be to study the action of ultra-violet rays obtained, for instance, by the uvioi-lamp of Messrs. Schott and Co., at Jena; that is, if the oxidation vessel is made of the same glass as that of the uvioi-lamp. These experiments are in a state of preparation.

Helder, Holland, June, 1905.

THE DETECTION OF METHYL ALCOHOL.*

By HEYWARD SCUDDER.

(Concluded from p. 141).

Reagent, Resorcin.

Mulliken-Scudder Test (*Ann. Chem. Journ.*, 1899, xxi., 266).—In its simplest form this consists in oxidising a dilute solution of the alcohol by plunging into it several times a spiral of copper wire heated to redness. The formaldehyde formed is tested for by adding one drop of a 0.5 per cent aqueous solution of resorcin, and pouring, without mixing, on top of a little concentrated sulphuric acid in a test-tube. A contact ring and, on very gentle shaking, flocks of a characteristic red colour appear, if formaldehyde is present. Acetaldehyde gives a ring and flocks of a colour that varies from yellow to brown. This shows 8 to 10 per cent of methyl alcohol in ethyl. The time required is about five minutes.

The modified form is more delicate (Mulliken, Scudder, *Ibid.*, 1900, xxiv., 444). The oxidation is carried out in the same way, but the acetaldehyde is removed by boiling the solution down about one-half. This may be done over a free flame for rapid work. In boiling down, some formaldehyde is always lost, and the more rapid the boiling the greater the loss. Therefore, it is advisable to boil down at 25–30° under diminished pressure in order to get the best results. Where little formaldehyde is present the formation of flocks is slow, so in this modified form after the solution is brought in contact with the sulphuric acid it must be allowed to stand for three minutes, then shaken very gently for a minute, causing the two liquid surfaces in contact to mix, but not allowing rapid or

* Percentage of nitrogen respectively 3.27, 3.27, 3.9, and 3.9.

† The fact that a solution of potassium iodide, which is indeed a destroyer of ozone, does not affect the boundary pressure, is important in connection with the opinion of Schönbein, Centnerszwer, and Bodländer, who point out that several of the substances which have considerable influence are known destroyers of ozone.

‡ Corrected for 5.4 per cent of nitrogen.

* Presented before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, July, 1905.

excessive mixing. If only a very little formaldehyde is present, rapid mixing prevents the formation of flocks, although it has little or no bad effect when much formaldehyde is present. The formation of flocks is a necessary part of the test, a contact ring of the proper colour not being considered sufficient evidence, since acetone and dimethyl-ethylcarbinol both give red contact rings. Methyl esters and ethers, methylal, and secondary and tertiary butyl alcohols give the same reaction as methyl alcohol in this test. This would indicate that whenever a methyl group and oxygen are close together and not bound firmly to the remainder of a compound, oxidation may produce formaldehyde, the amount formed probably being dependent on the relative attraction between the different groups in the compound. This test shows 2 to 3 per cent methyl alcohol in ethyl. The time required is about twenty minutes. One great advantage of the test is that the formation of flocks of characteristic colour gives a very positive indication, much more so than the production of a contact ring or of a temporary colour.

United States Pharmacopœia Test.—Sadler states that the committee for the revision of the Pharmacopœia found resorcin more delicate than phloroglucin as a test for the formaldehyde produced in the oxidation of methyl alcohol (*Am. Journ. Pharm.*, 1905, lxxvii., 106). They give the following directions:—Ten c.c. of the solution to be tested, having a concentration of about 10 per cent (in testing liquors or alcohol, the proper dilution must be made), are placed in a test-tube surrounded by cold water. It is oxidised by plunging a red-hot spiral of copper wire—of specified dimensions—to the bottom of the test-tube and holding it there one to two seconds. This is repeated five to six times. The filtered solution is boiled gently till any odour of acetaldehyde ceases to be clearly distinguishable. To the cooled solution one drop of a 1:200 aqueous solution of resorcin is added, and the mixture is floated on top of concentrated sulphuric acid in a test-tube. After standing three minutes the tube is gently rotated. If no rose-red ring appears, less than 2 per cent of methyl alcohol is present. The time required for the test is about fifteen minutes.*

Mulliken Test ("Provisional Methods for Analysis of Foods," U.S. Dept. Agriculture, Bureau Chemistry, *Bull.* 65, 73, 1902).—The alcohol is oxidised by a heated copper spiral, ammonia is then added, and the solution is boiled gently in a dish till the odour of ammonia has disappeared. The acetaldehyde is thus driven off and the formaldehyde is converted into hexamethylenetetramine. Concentrated hydrochloric acid is then added, and the solution brought momentarily to boiling to decompose the hexamethylenetetramine. The formaldehyde set free is tested for by resorcin as in the Mulliken-Scudder test. The test shows 10 per cent methyl alcohol in ethyl, and an expert is said to be able to detect less than this amount.

This test is no more delicate than the simple form of the Mulliken-Scudder test, so that its advantage is not apparent. Theoretically, the method is one that promises well. Ammonia unites with formaldehyde very rapidly to form hexamethylenetetramine, a compound that is stable on boiling, and does not distil off to any extent, while acetaldehyde-ammonia is decomposed by heat, and the acetaldehyde can be completely driven off by boiling. There are two defects in the process that I have not been able to overcome in any way. The addition of ammonia retains all the formaldehyde produced in the oxidation of ethyl alcohol, so that any delicate test applied after the decomposition of the hexamethylenetetramine, whether the test is for the formaldehyde or for the ammonia, is given both by ethyl and methyl alcohol. The oxidation

by a copper spiral does not produce enough formaldehyde from methyl alcohol to allow as a test the use of the formation of some compound of hexamethylenetetramine, such as the tetraiodide or the mercuric chloride compound, although both these compounds (which give difficultly soluble precipitates) can be used to detect the presence of quite small quantities of hexamethylenetetramine. No precipitate is formed from quantities of hexamethylenetetramine sufficient to give, after decomposition by boiling with acid, fairly thick flocks in the resorcin test. In this decomposition some formaldehyde is always lost, since other compounds besides ammonia and formaldehyde are formed. It is advisable to boil for fifteen or twenty seconds or longer to get the maximum amount of formaldehyde.

Reagent, Fuchsin.

Another use of hexamethylenetetramine gave promise, but fails at times for reasons that I cannot discover. The solution is oxidised by a heated copper spiral, filtered, an excess of ammonia added, and then boiled down about two-thirds. It is then cooled and 2 c.c. of fuchsin aldehyde reagent added. The sulphurous acid in this decomposes the hexamethylenetetramine and the aldehyde set free instantly colours the solution. A blank of pure water and fuchsin reagent is made, and the difference in colour and the time noted. In this way it was possible to show 1 per cent methyl alcohol in ethyl in fifteen minutes. But at times pure ethyl alcohol would give a colour as deep and as rapidly formed as that from methyl alcohol. As a rule ethyl alcohol when oxidised gives a colour that is very faint at first, and does not deepen for so long a time that the distinction between it and that from methyl alcohol is sufficiently marked to make a good test.

Reagent, Phloroglucin.

Acetaldehyde in amounts less than 0.01 per cent gives no reaction with an alkaline solution of phloroglucin in the Haigh and the Prescott tests, but will give a reaction with 1.0 c.c. or 2.5 c.c. of alkaline phloroglucin as used in the Sanglé-Ferrière test. In large quantities—over 0.1 per cent—it will also give a colour with the phloroglucin solution in the Haigh test. Formaldehyde in very small amounts gives a colour permanent for several minutes. The colour is said to be pure red. Actually it depends on the relative concentrations of the formaldehyde and the phloroglucin, varying from yellowish red through pure red to violet-red. Since, in any solution to be tested, the quantity of methyl alcohol present may be anywhere from 1 per cent to 100 per cent, oxidation will produce a very variable amount of formaldehyde, but the conditions of any test call for a fixed amount of phloroglucin; so the colour may be pure red or may be any of the shades mentioned.

Sufficient formaldehyde is formed in the oxidation of ethyl alcohol to give a colour with phloroglucin, though this colour is fainter than that obtained from the oxidation of solutions containing over 10 per cent of methyl alcohol. The colour is said to differ in quality from that obtained from oxidised methyl alcohol. I have not found this statement to be true, for the reason just given.

The colour obtained from oxidised methyl alcohol is said to be much more permanent than that given by oxidised ethyl alcohol. While this is true, the colour given by ethyl alcohol often lasts for a number of minutes, so that it is impossible to distinguish between ethyl and methyl alcohol either by this criterion or by the difference in colour, without making a comparative test with ethyl alcohol. In some experiments on the duration of the colour (the oxidant was a heated copper spiral), a 10 per cent aqueous solution of methyl alcohol gave a red that lasted for ten minutes without any noticeable fading; then it gradually grew lighter. At the end of twenty minutes the colour was still well marked. At the end of one hour there was no colour. A 20 per cent aqueous solution of ethyl alcohol gave a distinct red that lasted for six minutes, then began to fade. At the end of fifteen minutes the colour was very faint. A 20 per cent aqueous solution of a mixture of

* When I read this paper, I gave the outlines of a rapid test that would show 2 per cent methyl alcohol in ethyl. Since that time Sadler has published the test just given. The procedure of my test differed in several points, but the two are so much alike that it seems inadvisable to burden the literature with the details of mine. The fact that with such differences in procedure the results obtained are the same, shows that the Pharmacopœia test can be recommended to persons of limited chemical experience.

2 parts methyl alcohol and 98 parts ethyl alcohol, boiled down one-half after oxidation, gave a red that was deep for one minute, then faded, but was noticeable for more than ten minutes. A 20 per cent solution of ethyl alcohol similarly treated gave a colour that faded from the beginning and was hardly noticeable after three minutes.

The full depth of colour is sometimes not reached for one to two minutes. The duration of the colour is lessened by stirring.

When the solution is boiled, the colour changes to a clear brown-yellow. This same colour develops on boiling solutions that have become colourless. When cooled, after boiling, the colour from methyl alcohol is permanent for one to two minutes, then fades more or less slowly, while the colour from ethyl alcohol becomes very faint or disappears as soon as the solution is cold. This disappearance or fading of colour in the case of ethyl alcohol is noticed with certainty only when an excess of alkali is added, since the phloroglucin solution as ordinarily prepared will give, after boiling, a faint violet in the cold. The excess of alkali destroys this violet colour. When there is doubt as to the presence of methyl alcohol, on account of the faint or transient colour obtained by the ordinary test with phloroglucin in the cold, the question can often be settled definitely by the addition of an excess of alkali, boiling, and noting the depth and permanence of the colour of the cold solution.

Whenever phloroglucin is used as the agent to detect formaldehyde in testing for methyl alcohol, a comparative test with pure ethyl alcohol must always be made, since it is impossible to state definitely the exact colour or the exact duration of the colour that will be obtained from varying quantities of methyl alcohol. In making this comparative test each solution must be added to the phloroglucin solution at the same time, so that the intensity and permanence of the colours may be judged by direct comparison.

Prescott Test (Pharm. Archiv., 1901, iv., 86).—In this test the alcohol is oxidised by a heated copper spiral, hydrogen peroxide is added to destroy the acetaldehyde, the excess of hydrogen peroxide is removed by sodium thiosulphate, and the formaldehyde tested for by phloroglucin. This shows 5 per cent methyl alcohol in ethyl. It is difficult to get correct results with this test, because the action of the hydrogen peroxide and the thiosulphate seems to go wrong at times. The Haigh test is much more satisfactory.

Haigh Test (Pharm. Review, 1903, xxi., 404).—In this test the alcohol is oxidised by a heated copper spiral, the acetaldehyde removed by boiling the filtered solution till little or no odour is left, and the phloroglucin test used to show the presence of formaldehyde. The colour from methyl alcohol is said to last two to three minutes, that from ethyl alcohol to be faint and quickly to disappear. This shows 5 per cent methyl alcohol in ethyl. The time required, including the blank of ethyl alcohol, is about fifteen minutes.

The test is as satisfactory as any that uses phloroglucin. By adding alkali and heating the solution after it has been mixed with the phloroglucin (as previously described) it is possible to show 3 per cent to 4 per cent methyl alcohol by this test. The fact noted by Haigh that after one-half hour to one hour the solution from ethyl alcohol gives a blue colour, is due in my opinion to the phloroglucin alone (possibly the colour comes from some oxidation reaction), and has nothing to do with ethyl alcohol or its oxidation products.

Since acetaldehyde in small amounts gives no colour with alkaline phloroglucin, the question naturally arises, what is the reason for its removal in the Prescott and the Haigh tests? The answer is very simple—there is no need of removal. The working of the test has been misunderstood. When ethyl alcohol is oxidised, sufficient formaldehyde is produced to give a fairly deep and permanent colour with alkaline phloroglucin solution, which is quite a delicate reagent for the detection of formaldehyde. The

processes employed for the removal of acetaldehyde remove at the same time so much formaldehyde that the reaction with phloroglucin is reduced to a minimum. When methyl alcohol is present, sufficient formaldehyde is left to give a well-marked reaction. The experiments on the duration of colour, given under the general treatment of the phloroglucin reaction, show this very clearly.

Sanglé-Ferrière-Cumiasse Test (Ann. Chim. Anal. Appl., 1903, viii., 82).—This consists in oxidation of a cold dilute solution by potassium permanganate and sulphuric acid. The excess of permanganate is reduced by tannin, the solution is made faintly alkaline, and the manganese dioxide filtered off. The filtrate is tested by alkaline phloroglucin. It is said to show 1 per cent methyl alcohol in ethyl.

The test has a simple procedure, but the length of time necessary to oxidise the alcohol in order to get satisfactory results seems to vary with the room temperature, the amount of alcohol present, and the method of adding the sulphuric acid. The recommendation is made to confirm the test by acidifying and testing with gallic acid. This confirmation I regard as valueless, because of the great delicacy of the gallic acid test for formaldehyde. Ethyl alcohol often gives with phloroglucin quite a deep colour, not the faint colour mentioned in the description of the test.

Choice of Tests.

This will vary with circumstances. Unless there is supposed to be only a very small amount of methyl alcohol present, I should recommend trying first the simple Mulliken-Scudder test, which shows 8 per cent to 10 per cent and takes but a few minutes; next the Pharmacopœia test, which shows 2 per cent and takes fifteen minutes. If that gave no indication at all, the Trillat test should be used, but if there was any indication of the possible presence of methyl alcohol or a suspicion that it was there, I should advise rather than use the Trillat test to concentrate by distillation through a Hempel tube or Le Bel-Henninger tube or some such device, and then to use one of the shorter tests. This can be done much more quickly and easily than most persons suppose. In experiments to test the efficiency of the process when only small amounts of liquid are available, I used 25 c.c. of a mixture of 1 per cent methyl alcohol and 99 per cent ethyl alcohol. This was fractionated through a Hempel tube made of a glass tube 22.5 c.m. long, 1.7 c.m. in diameter, filled with glass beads about 3 m.m. in diameter. The beads held about 3½ c.c. of liquid that would not drain back into the flask. Three fractionations were made, taking the first time 15 c.c., then 7½ c.c., and finally 2 c.c. One c.c. of this last fraction was diluted, oxidised by a heated copper spiral, boiled down one-half over a free flame, and tested by resorcin. Moderately thick red flocks appeared. The total time consumed was one hour (this includes the time taken in allowing the liquid to drain back into the flask, a procedure necessary when such small quantities of liquid are being fractionated in this way). The Trillat test would have taken five hours. The Sanglé-Ferrière-Cumiasse test is claimed to have a delicacy sufficient to show this amount of methyl alcohol, but I am doubtful about its indications. None of the other tests is sufficiently delicate to use in such a case.

The great value of the resorcin test is in the positive evidence given and the advantage of having some idea in a rough way of the quantity of formaldehyde present. The formation of flocks of characteristic colour shows positively the presence of a certain amount of formaldehyde, and no comparative test with ethyl alcohol is necessary. If there is only a contact ring and no flocks, there is very little formaldehyde present. When more is present there will be scanty small flocks. When much is present, the flocks are thick and abundant.

Mixtures.

In consequence of the great number of organic compounds, it is impossible to devise a test that will show a particular compound in any possible mixture. Certain general principles can be given, and by the aid of these and by a

clear understanding of what the test used will show and what are its possibilities of error, the detection of methyl alcohol ought to be certain except when it is present in very small quantities, and there is not sufficient material to allow of concentration.

If formaldehyde is present, it must be removed, if any of the oxidation tests are used, since they are all dependent on conversion of the alcohol to formaldehyde or methylal. This may be accomplished by digestion with ammonia; by digestion cold with excess of sodium bisulphite for four to five hours (Bamberger, *Zeit. Angew. Chem.*, 1904, xvii., 1246); by digestion at 70–80° in a stoppered bottle with resorcin and sulphuric acid for two to three hours (Mulliken, Scudder, *Amer. Chem. Journ.*, 1900, xxiv., 449); or by boiling with a return condenser with aniline and phosphoric acid (Allen, Chattaway, *Analyst*, 1891, xvi., 113). The liquid is then distilled, the formaldehyde remaining behind in combination. The distillate should always be tested for aldehyde to make sure that the removal is complete. Other means that may prove useful in certain cases are digestion hot with sodium sulphite (Lemme, *Chem. Zeitung*, 1903, xxvii., 896), or with hydrazine sulphate (Pfaff, *Chem. Zeitung*, 1902, xxvi., 701). When difficulty is found in removing all the formaldehyde, it is often possible without further treatment to make a rapid test which either will show the presence of methyl alcohol or will make further investigation desirable. Under these conditions little formaldehyde will be present, and the resorcin test used before oxidation will show only a contact ring. When the solution is oxidised and the resorcin test again applied, if methyl alcohol is present, the increased amount of formaldehyde will be shown either by the presence of flocks or by thickening of the ring. The presence of flocks in such a case would be almost conclusive evidence of the presence of methyl alcohol. Fractional distillation is often of great help in such cases. Gnehm and Kaufler (*Zeit. Angew. Chem.*, 1905, xviii., 93) state that in the estimation of methyl alcohol in formaldehyde, when the formaldehyde is condensed with sodium sulphanilate, and the alcohol distilled off, the distillate always contains small quantities of compounds having the characteristic odour of formaldehyde and the power of reducing silver nitrate, but that these compounds are unsaturated bodies of unknown nature.

Other aldehydes can be removed by digestion with resorcin and sulphuric acid, or with aniline and phosphoric acid. Their presence is indicated by the usual aldehyde reactions or by the resorcin test.

Phenols and bases will combine with any formaldehyde that may be made in the course of a test. They must therefore be removed—by distillation from sodium or potassium hydroxide in the case of phenols (this treatment also removes acids)—by distillation from dilute sulphuric acid in the case of bases.

Various compounds such as colouring-matters, &c., can be removed by simple or fractional distillation, by filtration through bone-black with or without previous treatment by lime, or by extracting the alcohol with water and testing the aqueous extract after distillation.

It is best to test only solutions wholly soluble in two to three parts of water, that will distil between 50° and 100°.

Thermo-chemistry of Hydrazones.—Ph. Landrieu.—The author finds that the heat evolved during the action of the acetones and aldehydes on phenylhydrazine is practically constant; it varies between 12 cal. and 16 cal. This number is slightly higher than that obtained during the reaction of the aldehydes or acetones on hydroxylamine with formation of oximes, the latter having the value 10 cal. to 13 cal. This explains the displacement of hydroxylamine by phenylhydrazine and the formation of hydrazone.—*Comptes Rendus*, cxli., No. 6.

* Mulliken, Scudder (*Amer. Chem. Journ.*, xxiv., 447). The question is here treated entirely from the standpoint of the resorcin test, but the general principles remain the same.

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. SCHEME FOR EXAMINATIONS IN TECHNICAL CHEMISTRY.

THE Scheme for Examinations in Technical Chemistry which the Council of the Institute has decided to adopt should tend to promote the efficiency of chemists in works, though it is obvious that the qualifications to pass such examinations can only be obtained by actual practice in the works themselves.

Examinations are, at the best, a clumsy way of sorting the capable from the incapable men, and we are not inclined to think that a written examination is the best means for picking out the men best qualified in purely practical work. However, until some better method is devised we must needs fall back on the barbarous means at present in use.

The following is the gist of the scheme about to be adopted by the Council of the Institute of Chemistry:—

1. The Council has resolved to hold examinations in the industrial applications of chemistry and to grant certificates in respect thereof.
2. These examinations will be open only to Fellows, and to those Associates who have been registered as such for at least one year.
3. Candidates will be required to produce evidence of practical technical training.
4. The examinations will comprise the following:—
 - a. The application of well-known chemical and physical laws to industrial operations.
 - b. The development, control, and transmission of power and heat.
 - c. A working knowledge of operations and plant of which general use is made in industrial works for the treatment and handling of materials, finished products, waste products, and effluents, including a practical acquaintance with fittings and stores.
 - d. The properties of materials affecting their application to the construction of plant and apparatus in chemical works.
 - e. Some ability in interpreting drawings of chemical plant and in making dimensioned rough sketches.
 - f. The calculation of working costs, and a general knowledge of the clerical work connected with manufacturing operations.
5. Each candidate will be required to select one important industry in which his knowledge of the above subjects may be tested. Questions which might involve the disclosure of unpublished processes and details of plant in particular works will not be asked. All candidates will be expected to give evidence of a general knowledge of chemical technology. The Examiners will take into account original work and special knowledge, but not so as to excuse the candidate from any part of the examination.

In making this scheme the basis for examinations in technical chemistry, the Council wishes generally to indicate the knowledge a candidate should possess. The Fellow or Associate, who by his previous examinations and work has proved that he possesses the theoretical knowledge necessary for his profession, and is efficient in practical laboratory work, should at this examination show that he has learnt the industrial application of his science, and has by practical experience acquired the habit of thinking and working industrially. He should show a practical knowledge of operations, both chemical and mechanical, and of the apparatus and machinery commonly used in chemical manufactures. He should be a chemist, with so much knowledge of chemical technology and engineering, that he can intelligently and economically supervise manufacturing operations, and that, when suggesting improvements or new manufactures, he can advise as to the apparatus and machinery required. He should be able "to think in tons," and know how profits are made.

Fellows and Associates desiring to take the examination

will be required to produce evidence of practical technical training distinct from the course for the Associateship. Experience of not less than one year in practical manufacture, or an equivalent amount of training, would constitute evidence satisfactory to the Council, who will be prepared, at first, to interpret Clause 3 very broadly.

The Council desires to encourage young chemists to take post-graduate training and to gain practical experience; also, to urge universities and technical colleges to establish special courses, under teachers of experience and in suitably equipped workshops, for instruction in chemical technology. Steps in this direction are being taken in various parts of the country, and in some instances provision is being made for teaching the methods of applied chemistry on a fairly large scale.

The form of the examinations, the exact dates when the first examination shall be held, the time it shall occupy, the fee, and other details will be published in due course.

NOTICES OF BOOKS

The Crystallisation of Iron and Steel. By J. W. MELLOR, D.Sc. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THIS book contains a course of six lectures delivered to the engineering students of the Staffordshire County Technical Classes at the Newcastle High School in November and December, 1904, and gives a summary of the most important results which have been obtained recently with regard to alloys of iron and steel. The first lecture discusses the solidification and cooling of alloys, and from it the student should be able to acquire very readily clear and accurate ideas concerning transition temperatures, cooling curves, &c. The second lecture deals with the constituents of iron and steel and the phase rule, the numerical examples which are interspersed being of great value in establishing the student's knowledge, and showing him how to apply it practically. The hardening, annealing, and tempering of steel and the influence of stress and strain are treated in the most graphic manner in subsequent lectures, which are all well illustrated, and contain copious references for those who wish to pursue the subject further. The last lecture deals with the preparation of a specimen for the microscope, and gives a rough estimate of the time required to obtain a microphotograph of the structure of a metal, and also of the outfit required for this purpose and its approximate cost. An appendix contains a glossary of terms, and in many cases gives their French and German equivalents, and is not the least useful feature of a thoroughly practical book, which illustrates the author's power of inspiring interest and instilling a knowledge of facts simultaneously.

Higher Mathematics for Students of Chemistry and Physics.

By J. W. MELLOR, D.Sc. Second Edition. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THE new edition of this most useful book has been rewritten, and while the general plan is unaltered some changes have been made in the details of the arrangement, and fuller explanations are given of points which appear to present special difficulties. Some new sections are added, e.g., on the theory of the washing of precipitates, the tests for the convergency of series, and the calculus of variations. All the alterations which have been made serve to increase the value of the book, which has been much appreciated both by students and teachers.

The Theory of Experimental Electricity. By WILLIAM CECIL DAMPIER WHETHAM, M.A., F.R.S. Cambridge: University Press. 1905.

THE study of this work cannot fail to develop in the student an interest in the problems of electricity, for the

author has recognised the great value of giving his readers an insight into research, so that they may realise that the science is still in a state of growth. Thus he does not hesitate to touch upon debatable points and to dwell shortly upon hypotheses which very likely will not stand the test of future developments; he alludes to work which is now being done, and does so in such a way as to stimulate the desire for more knowledge, and to show the student how to acquire it most easily and satisfactorily. The book hardly takes the place of an ordinary text-book of electricity, and, indeed, was written more especially as a supplement and book of reference for the author's own students who were attending a course of lectures upon the elementary theory of electricity. It is not a cram book suitable for the use of examination candidates, but is rather a scholarly exposition of the subject, having a considerable literary value. Certain branches which have seen special development recently, such as electrolysis, conduction through gases, and radio-activity, are treated rather more fully than in the usual text-books, and the chapters on these subjects contain the essentials most lucidly and interestingly treated.

Outlines of Physiological Chemistry. By S. P. BEEBE, Ph.D., and B. H. BUXTON, M.D. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1904.

THIS book attacks the subject of physiological chemistry only from the theoretical side, and deals almost exclusively with the chemistry of certain compounds which are of physiological interest. A knowledge of inorganic chemistry is assumed, but the theory of solutions is briefly discussed, and nearly half the book is devoted to the consideration of elementary organic chemistry, illustrated chiefly by substances which are of importance in physiology. The remainder of the book deals with the composition and properties of the proteids and the enzymes. The chemistry of the secretions of the animal body, of the tissues, and of respiration are subjects which are omitted, although room is found for a chapter on disease and immunity. Thus it will be seen that the book forms rather a preparation for the study of physiological chemistry, and even from this point of view it is hardly satisfactory, for the student would be able to find practically all that is in the first part of the book in a text-book of organic chemistry, and, moreover, would require a more extended knowledge of the subject before attacking physiological chemistry. The work suffers throughout from a want of cohesion and system, and is exceedingly sketchy in places, suggesting notes jotted down more or less at random.

A Primer of Explosives. By Major A. COOPER-KEY. Edited by Captain J. H. THOMSON. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1905.

THIS little book is intended for the use of local inspectors and dealers, and is not a scientific treatise on explosives. It is consequently written in untechnical language, and really constitutes a brief commentary on the Explosives Act. A description is given of the nature of an explosive, and the composition and use of each class of explosive, as classified in the Order in Council made under Section 106 of the Act, are discussed, special stress being laid upon the dangers attending the use of each class. The last chapter contains suggestions on the storing of explosives, precautions to be observed, and the safest methods for destroying gunpowder and all blasting materials.

A Treatise on Chemistry. By Sir H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Volume I. *The Non-metallic Elements.* Third Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1905.

IN preparing for the press the third edition of this treatise Sir Henry Roscoe, assisted by Drs. H. G. Colman and A.

Harden, has carefully revised the text in order to bring it thoroughly up to date. Every effort in the way of consulting the most recent authoritative literature appears to have been made to render the work as complete and trustworthy as possible, and, as in the earlier editions, special attention has been paid to the description of such technical processes as the manufacture of sulphuric acid and of coal-gas. The pages on the atmosphere may be specially mentioned as forming an excellent example of how a subject may be presented with perfect scientific accuracy and considerable attention to detail, and yet in such a manner as to excite interest to the fullest degree.

Sugar and the Sugar-cane. By NOEL DEERR. Altrincham (Manchester): Norman Rodger. 1905.

THIS work aims at covering a large field, for in it is given a complete account of the sugar industry, from the agriculture of the cane to the analysis of sugar-house products. The treatment of such a range of subjects within a limited space necessitates the sacrifice to a certain extent of some branches, and in this case it is chiefly the scientific aspect which has suffered, although it is not by any means altogether neglected. The author has studied the standard works on the sugar-cane, and, moreover, gives his readers the benefit of the conclusions to which he himself has come, as regards many practical details, after years of experience. These personal opinions are in themselves of no mean value. Besides discussing the cultivation of the cane and the extraction and treatment of the juice, the author enters at some length upon the question of the control of the factory, considering it more especially from the point of view of those factories in which a chemist is not employed, and in which the apparatus and fittings are reduced to the minimum absolutely necessary for sugar analysis only.

Methods of Chemical Control in Cane-sugar Factories. By H. C. PRINSEN GEERLIGS. Altrincham (Manchester): Norman Rodger. 1905.

THE greater part of the matter in this book has already been published in the *International Sugar Journal*, 1904, vol. vi., and now appears in book-form with the addition of many tables which are constantly required for reference in the sugar laboratory. The work contains directions for the laboratory work, and calculations necessary to enable the chemist to draw up the usual detailed daily, and fortnightly or monthly reports; also a list of the instruments and utensils required, together with explicit instructions for verifying the measuring tanks and vessels, and it will form a valuable addition to the library of the chemist employed in sugar-works.

Leather for Libraries. By E. WYNDHAM HULME, J. GORDON PARKER, A. SEYMOUR-JONES, CYRIL DAVENPORT, and F. J. WILLIAMSON. London: The Library Supply Co. 1905.

THIS small book, published for the Sound Leather Committee of the Library Association, gives many useful hints for the benefit of librarians and others, and though some of its recommendations may be regarded somewhat in the light of counsels of perfection, undoubtedly many malpractices have crept into the process of preparing leather for the binder, and warnings on these points are well worth noting by those who are interested in book-binding. The question that rises naturally in the mind of the reader is whether it is much good to make efforts to ensure the durability of the outer coverings of books when the paper of which they are made has shown such marked deterioration lately. Be this as it may, the book will no doubt be read with interest; it contains thoroughly practical directions for the binding and repairing of books for public libraries, and chapters on the history of tanning, the causes of the decay of leathers, and the characteristics and values of modern book-binding leathers, six specimens of which are attached to the covers.

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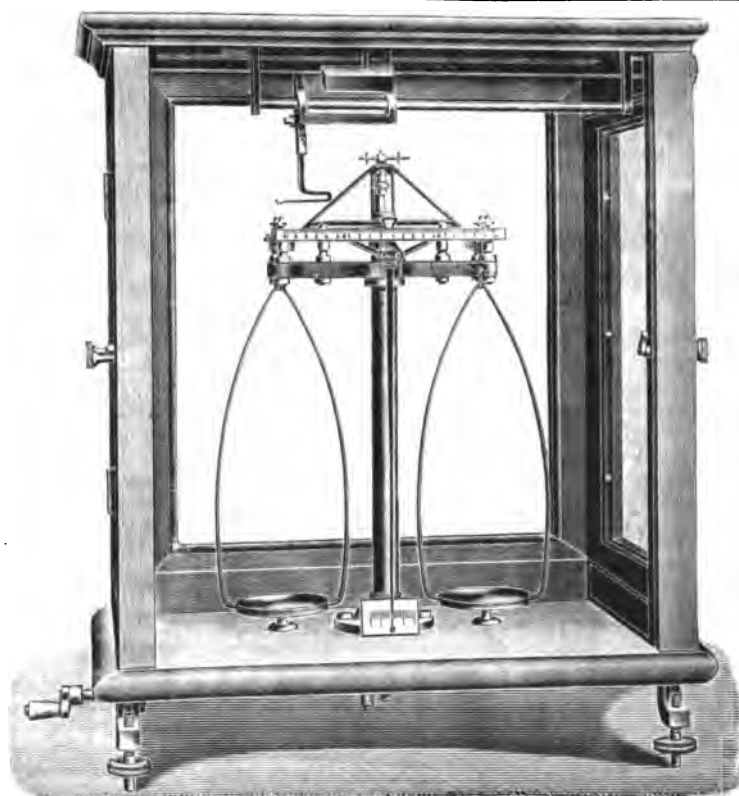
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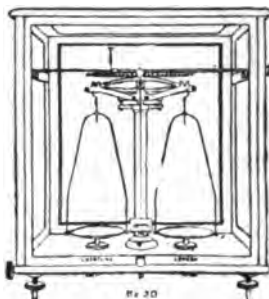
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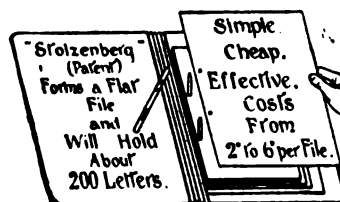
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THE CHEMICAL NEWS.

VOL. XCII., No. 2393.

DIAMONDS.

A LECTURE DELIVERED BEFORE THE BRITISH ASSOCIATION
AT KIMBERLEY, SEPTEMBER 5, 1905.

By Sir WILLIAM CROOKES,
Hon. D.Sc. (Oxford and Dublin), F.R.S.

(Concluded from p. 150).

Physics of the Diamond.

I WILL now briefly survey the chief chemical and physical characteristics of the diamond, showing you by the way a few experiments that bear upon the subject.

The black inclusions in some transparent diamonds consist of graphite. On crushing a clear diamond showing such spots and heating in oxygen to a temperature well below the point at which diamond begins to burn, Moissan found that the grey tint of the powder disappeared, no black spots being seen under the microscope. There also occur what may be considered intermediate forms between the well-known crystallised diamond and graphite. These are "boart" and "carbonado." Boart is an imperfectly crystallised diamond, having no clear portions, and therefore useless for gems. Boart is frequently found in spherical globules, and may be of all colours. It is so hard that it is used in rock-drilling, and when crushed it is employed for cutting and polishing other stones. Carbonado is the Brazilian term for a still less perfectly crystallised form of carbon. It is equally hard, and occurs in porous masses, and in massive black pebbles, sometimes weighing a couple or more ounces.

Crystallisation.

The diamond belongs to the isometric system of crystallography; the prevailing form is octahedral. It frequently occurs with curved faces and edges. Twin crystals (macles) are not uncommon.

On the table I have models of various crystalline forms of native diamonds.

No. 20. Diamond in the form of a hexakisoctahedron (the forty-eight scalenohedron), or a solid figure contained by forty-eight scalene triangles. According to Professor Maskelyne, this occurs as a self-existent form only in the diamond.

No. 59. Diamond in the form of a hexakisoctahedron and octahedron. From Sudafrika.

No. 105. Diamond in the form of octahedron with inter-sections.

No. 127. Diamond from Brazil.

No. 128. Diamond from Sudafrika.

No. 129. Diamond from Brazil.

A macle or twin crystal, showing its formation from an octahedron with curved edges.

The use of diamond in glass cutting I need not dwell on. So hard is diamond in comparison to glass, that a suitable splinter of diamond will plane curls off a glass plate as a carpenter's tool will plane shavings off a deal board. On the screen I show a few diamond-cut glass shavings.

Many crystals of diamonds have their surfaces beautifully marked with equilateral triangles, interlaced and of varying sizes. Under the microscope these markings appear as shallow depressions sharply cut out of the surrounding surface; these depressions were supposed by Gustav Rose to indicate the probability that the diamonds at some previous time had been exposed to incipient combustion. Rose also noted that striations appeared on the surfaces of diamonds burnt before the blowpipe.

I have tried many times to imitate these markings by partial combustion of clear crystals of diamond, but have not succeeded in reproducing triangles of such beauty as you

see formed by nature. According to the crystalline face exposed to incipient combustion the etchings are triangular or cubical, and sometimes intermediate between the two. I throw on the screen magnified photographs of these etchings, and you will observe that while the triangular or box like tendency is very apparent, there is an absence of regularity and sharpness.

The artificial markings are closer massed, looking as if the diamond during combustion had been dissected into triangular and rectangular flakes, while the markings natural to crystals appear as if produced by the crystallising force as they were being built up.

Certain artificial diamonds present the appearance of an elongated drop. I have seen diamonds which have exactly the appearance of drops of liquid separated in a pasty condition and crystallised on cooling. Diamonds are sometimes found with little appearance of crystallisation, but with rounded forms similar to those which a liquid might assume if kept in the midst of another liquid with which it would not mix. Other drops of liquid carbon retained for sufficient time above their melting-point would coalesce with adjacent drops, and on slow cooling would separate in the form of large perfect crystals. Two drops, joining after incipient crystallisation, might assume the not uncommon form of interpenetrating twin crystals. Illustrations of all these caprices are here to-night.

Again, diamond crystals are generally perfect on all sides. They show no irregular side or face by which they were attached to a support, as do artificial crystals of chemical salts; another proof that the diamond must have crystallised from a dense liquid.

Having no double refraction the diamond should not act on polarised light. But as is well known, if a transparent body which does not so act is submitted to strain of an irregular character it becomes doubly refracting, and in the polariscope reveals the existence of the strain by brilliant colours arranged in a more or less defined pattern according to the state of tension in which the crystal exists. I have examined many hundred diamond crystals under polarised light, and with few exceptions all show the presence of internal tension. I will project some diamonds on the screen by means of the polarising microscope, and you will see by the colours how great is the strain to which some of them are exposed. On rotating the polariser, the black cross most frequently seen revolves round a particular point in the inside of the crystal; on examining this point with a high power, we sometimes see a slight flaw, more rarely a minute cavity. The cavity is filled with gas at enormous pressure, and the strain is set up in the stone by the effort of the gas to escape. I have already told you that the great Cullinan diamond by this means reveals a state of internal stress and strain.

It is not uncommon for a diamond to explode soon after it reaches the surface; some have been known to burst in the pockets of the miners or when held in the warm hand, and the loss is the greater because large stones are more liable to explode or fly in pieces than small ones. Valuable stones have been destroyed in this way, and it is whispered that cunning dealers are not averse to allowing responsible clients to handle or carry in their warm pockets large crystals fresh from the mine. By way of safeguard against explosion, some dealers imbed large diamonds in raw potato to insure safe transit to England.

The anomalous action which many diamonds exert on polarised light is not such as can be induced by heat, but it can easily be conferred on diamonds by pressure, showing that the strain has not been produced by sudden cooling but by sudden lowering of pressure.

The illustration of this peculiarity is not only difficult, but sometimes exceedingly costly—difficult because it is necessary to arrange for projecting on the screen the image of a diamond crystal between the jaws of a hydraulic press, the illuminating light having to pass through delicate optical polarising apparatus—and costly because only perfect, clear crystals can be used, and crystals of this character sometimes fly to pieces as the pressure rises. No colour as yet

is seen on the screen, the crystal not being birefringent. A movement of the handle of the press, however, gives the crystal a pinch, instantly responded to by the colours on the screen, showing the production of double refraction. Another movement of the handle brightens the colours; a third may strain the crystal beyond its power of resistance, so I refrain.

Hardness.

Diamonds vary considerably in hardness, and even different parts of the same crystal differ in their resistance to cutting and grinding.

Beautifully white diamonds have been found at Inverel, New South Wales, and from the rich yield of the mine and the white colour of the stones, great things were expected. In the first parcel which came to England the stones were found to be so much harder than South African diamonds that it was at first feared they would be useless except for rock boring purposes. The difficulty of cutting them disappeared with improved appliances, and they now are highly prized.

The famous Koh-i-noor, when cut into its present form, showed a notable variation in hardness. In cutting one of the facets near a yellow flaw, the crystal became harder and harder the further it was cut, and after working the mill for six hours at the usual speed of 2400 revolutions a minute, little impression was made. The speed was increased to more than 3000, when the work slowly proceeded. Other portions of the stone were found to be comparatively soft, and hardened as the outside was cut away.

I can illustrate the intense hardness of the diamond by experiment. On the flattened apex of a conical block of steel I place a diamond, and upon it I bring down a second cone of steel. With the lamp I project an image of the diamond and steel faces on the screen, and force them together by hydraulic power. I can squeeze the stone into the steel blocks without injuring it in the slightest degree.

The pressure gauge shows (60) atmospheres, and the piston being 3.2 inches diameter, the absolute pressure is (3.16) tons, equivalent on a diamond of (12) square m.m. surface to (170) tons per square inch of diamond.

Although not directly bearing on the subject I will introduce the only serious rival of the diamond as regards hardness. It is the metal tantalum, a fine specimen of which I owe to Messrs. Siemens Brothers. A hole had to be bored through a plate of this metal, and a diamond drill was used revolving at the rate of 5000 revolutions per minute. This whirling force was continued ceaselessly for three days and nights, when it was found that only a small depression $\frac{1}{2}$ m.m. deep had been drilled, and it was a moot point which had suffered most damage, the diamond or the tantalum (W. von Bolton, *Zeitschr. Elektrochem.*, ii., 45-51, Jan. 20, 1905). In another respect tantalum is likely to rival graphitic carbon, as it has rivalled adamantite carbon. Its thin wire is extensively used for filaments of incandescent electric lamps; it shows a much higher efficiency than does the old carbon filament. The melting-point of tantalum is about 2300° C., a temperature seldom or never reached in an ordinary lamp.

Density.

The following table gives the specific gravities of the minerals found on the sorting tables:—

	Specific gravity.
Hard graphite	2.5
Quartzite and granite	2.6
Beryl	2.7
Mica	2.8
Hornblende	3.0
Boart	3.47-3.49
Carbonado	3.50
Diamond	3.514-3.518
Garnet	3.7
Corundum	3.9
Zircon	4.4
Barytes	4.5
Chrome and titanitic iron ore..	4.7
Magnetite	5.0

I have here a liquid, the double nitrate of silver and thallium, which while solid at ordinary temperatures, liquefies at 75° C., and then has a specific gravity of 4.5. Admixture with water lowers the density to any desired point.

In the projection apparatus I have a glass cell containing this liquid diluted to a density of about 3.6. I throw in pieces of the above named minerals, and you see all those whose density is lower than 3.6 rise to the surface, while the denser minerals sink. I now carefully add a little water and stir well, until I have reduced the density of the liquid to that of the diamond, when the heterogeneous collection sorts itself into three parts. The graphite, quartz, beryl, mica, and hornblende rise to the surface; the garnet, corundum, zircons, &c., sink to the bottom, while the diamonds float in the middle of the liquid. With a platinum landing net I skim off the swimmers and put them into one dish; with the same net I fish out the diamonds and put them in a second dish, while by raising a sieve at the bottom I remove the heavy minerals and put them into a third. The accurate separation of diamonds from the heterogeneous mixture has been effected in less time than has taken me to describe the experiment.

The table shows that diamonds vary somewhat in density among themselves, between narrow limits. Here is an illustration. I have a flat test-tube in which I have some of the same dense liquid, and in it are three selected diamonds. One rises to the top, another floats uncertain where to settle, rising and falling as I raise or lower the temperature of the sorting liquid, whilst the third sinks to the bottom. Allowing the liquid to cool a degree or two slightly increases the density and sends all three to the surface.

Refractivity.

But it is not the hardness of the diamond so much as its optical qualities that make it so highly prized. It is one of the most refracting substances in nature, and it also has the highest reflecting properties. In the cutting of diamonds advantage is taken of these qualities. When cut as a brilliant the facets on the lower side are inclined so that light falls on them at an angle of 24° 13', at which angle all the incident light is totally reflected. A well cut brilliant should appear opaque by transmitted light except at a small spot in the middle where the table and culet are opposite. All the light falling on the front of the stone is reflected from the facets, and the light passing into the diamond is reflected from the interior surfaces and refracted into colours when it passes out into the air, giving rise to the lightnings, the effulgence, and coruscations for which the diamond is supreme above all other gems.

I hold some cut diamonds in the electric light; by transmitted light you see they are black, while by reflected light they fill the room with radiance, dazzle, and colour.

The following table gives the refractive indices of diamonds and other bodies:—

Refractive Indices for the D Line.

Chromate of lead	2.50-2.97
Diamond	2.47-2.75
Phosphorus	2.22
Sulphur	2.12
Ruby	1.78
Thallium glass	1.75
Iceland spar	1.65
Topaz	1.61
Beryl	1.60
Emerald	1.59
Flint glass	1.58
Quartz	1.55
Canada balsam	1.53
Crown glass	1.53
Fluor-spar	1.44
Ice	1.31

In vain I have searched for a liquid of the same refraction as diamond. Such a liquid would be invaluable to the

merchant, as on immersing a stone the clear body would absolutely disappear, leaving in all their ugliness the flaws and black specks so frequently seen even in the best stones.

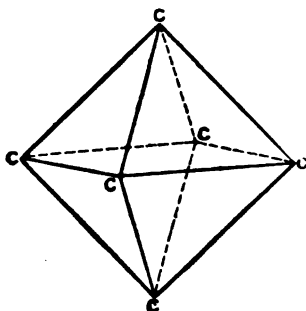
Arguing from theoretical considerations connected with the Specific Refractive Energy of diamond, and employing Lorentz's expression for refraction—

$$\left(\frac{\mu^2 - 1}{\mu^2 + 2} \right) \frac{P}{d},$$

in which μ = refractive index;
 $\mu - 1$ = refractive energy;
 d = density;
 P = molecular weight.

Brühl has shown that diamond is perfectly normal in its optical properties, and has an atomic refraction = 5. He has put forward the speculation that the diamond may be the last member of the paraffin series of which marsh-gas is the first.

"Now we can imagine," says Brühl (*Proceedings of the Royal Institution*, May 26, 1905), "why the diamond, i.e., pure crystallised carbon, is optically normal. We obtain an idea of the mineral's chemical constitution, and of the way in which the atoms of carbon are perhaps combined in the sparkling gem. The diamond cannot possibly contain any double bonds. Imagine, however, at each of the six corners of a regular octahedron, a single molecule of marsh-gas, CH_4 , i.e., altogether C_6H_{24} , and then imagine all the 24 hydrogen atoms successively removed, so that each carbon atom is connected with each of its neighbours only by a single bond, and thus all six atoms of carbon are united together in a single whole. Then you obtain, as the most simple representation of the molecule of the diamond, a regular octahedron, with one atom of carbon at each of its six corners, whilst the edges represent the mutual bonds:—



Several simple molecules of this kind may be combined into one crystallised particle of the spectrochemically normal diamond."

Absorption Spectrum of Diamond.

On passing a ray of light through a diamond and examining it in a spectroscope, B. Walter has found in all colourless brilliants of over one carat in weight, an absorption band at wave-length 4155 (violet). He ascribes this band to an impurity and suggests it may possibly be due to samarium. Three other fainter lines were detected in the ultra-violet by means of photography.

Phosphorescence of Diamond.

After exposure for some time to the sun many diamonds glow in a dark room. Some diamonds are fluorescent, appearing milky in sunlight. In a vacuum, exposed to a high-tension current of electricity, diamonds phosphoresce of different colours, most South African diamonds shining with a bluish light. Diamonds from other localities emit bright blue, apricot, pale blue, red, yellowish green, orange, and pale green light. The most phosphorescent diamonds are those which are fluorescent in the sun. One beautiful green diamond in my collection, when phosphorescing in a

good vacuum, gives almost as much light as a candle, and you can easily read by its rays. But the time has hardly come when diamonds can be used as domestic illuminants! The emitted light is pale green, tending to white, and in its spectrum, when strong, can be seen bright lines, one at about λ 5370 in the green, one at λ 5130 in the greenish blue, and one at λ 5030 in the blue.

After many years' bombardment in a vacuum tube this diamond grew very dark, almost black on the surface. Heating in a mixture of nitric acid and potassium chlorate scarcely changed the colour. The action of heat was then tried, and on slowly heating to about 500° C. the dark colour entirely disappeared, and the original milky green appearance was restored. Although I watched narrowly I could see no trace of phosphorescence during the heating.

Diamonds which phosphoresce red generally show the yellow sodium line superposing on a continuous spectrum. In one Brazilian diamond phosphorescing a reddish yellow colour, I detected the citron line characteristic of yttrium.

By permission of Mrs. Kunz, wife of the well known New York mineralogist, I will show you perhaps the most remarkable of all phosphorescing diamonds. This prodigy diamond will phosphoresce in the dark for some minutes after being exposed to a small pocket electric light, and if rubbed on a piece of cloth a long streak of phosphorescence appears.

The rays which make the diamond phosphoresce are high in the ultra-violet. A thin sheet of glass cuts them all off. To illustrate this phosphorescence under the influence of the ultra-violet rays, I have arranged a powerful source of these rays, and in front I expose a design made up of certain minerals—willemite, franklinite, calcite, &c.,—phosphorescing of different colours. Their brilliant glow ceases entirely when I interpose a thin piece of glass between them and the ultra-violet lamp.

Tribo-luminescence.

A few minerals give out light when rubbed, and Mrs. Kunz's diamond is equally striking in this respect. In the year 1663 the Hon. Robert Boyle read a paper before the Royal Society, in which he described several experiments made with a diamond which markedly showed tribo-luminescence. As specimens of tribo-luminescent bodies I show you sphalerite (sulphide of zinc) and an artificial sphalerite, which is even more responsive to friction than the native sulphide.*

Combustion of the Diamond.

When heated in air or oxygen to a temperature varying from 760° to 875° C. according to its hardness, the diamond burns with production of carbonic acid. It leaves an extremely light ash, sometimes retaining the shape of the crystal, consisting of iron, lime, magnesia, silica, and titanium. In boart and carbonado the amount of ash sometimes rises to 4 per cent, but in clear crystallised diamonds it is seldom higher than 0.05 per cent. By far the largest constituent of the ash is iron.

The following table shows the temperatures of combustion in oxygen of different kinds of carbon:—

	°C.
Condensed vapour of carbon	650
Carbon from sugar, heated in an electrical furnace	660
Artificial graphites, generally	660
Graphite from ordinary cast-iron	670
Carbon from blue ground, of an ochrey colour	690
" " " " " very hard and black	710
Diamond, soft Brazilian	760
" " " " " hard Kimberley	780
Boart from Brazil	790
" " " " " from Kimberley	790
" " " " " very hard, impossible to cut	900

* Artificial tribo-luminescent sphalerite:—

Zinc carbonate	100 parts
Flower of sulphur	30 "
Manganese sulphate	1 per cent

Mix with distilled water and dry at a gentle heat. Put in luted crucible and keep at a bright red heat for from two to three hours.

Action of Radium on Diamond,

The β -rays from radium having like properties to the stream of negative electrons in a radiant matter tube, it was of interest to ascertain if they would exert a like difference on diamond. The diamond glows under the influence of the β -radiations, and crushed diamond cemented to a piece of card or metal makes an excellent screen in a spinthariscopes—almost as good as zinc sulphide. Some fine colourless crystals of diamond were embedded in radium bromide and kept undisturbed for more than twelve months. At the end of that time they were examined. The radium had caused them to assume a beautiful blue colour, and their value as "fancy stones" had been materially increased. Here are a couple of diamonds originally of the same purity of water. One has been coloured by radium, the other is in its natural state. The colour of the radium tinted stone is very pronounced. The lantern slide shows the darkening thus produced. A and B are diamonds after twelve months burial in radium bromide; diamond C is of the original colour.

This blue colour is persistent and penetrates below the surface. It is unaffected by long continued heating in strong nitric acid and potassium chlorate, and is not discharged by heating to redness.

To find out if this prolonged contact with radium had communicated to the diamond any radio-active properties, six diamonds were put on a photographic plate, and kept in the dark for a few hours. I will project the image of the result after development. The three on the upper row are the diamonds which have had a prolonged sojourn with radium, the three below are similar diamonds picked out for comparison, which have not been near radium. See how strangely the three upper ones have acted. Notice also that by mere contiguity to the others the lower diamonds also shine with an induced, factitious radio-activity. I throw on the screen a magnified image of one of the blue crystals, and you see in how regular and geometrical a pattern the radio-active emanations radiate from the crystal. This observation has only been made a short time, and is still under investigation. Like the blue tint the radio-activity persists after drastic treatment. To me this proves that radio-activity does not merely consist in the adhesion of electrons or emanations given off by radium, to the surface of an adjacent body, but the property is one involving layers below the surface, and like the alteration of tint is probably closely connected with the intense molecular excitement the stone had experienced during its twelve months' burial in radium bromide.

A diamond that had been coloured blue by radium, and had acquired strong radio-active properties, was slowly heated to dull redness in a dark room. Just before visibility a faint phosphorescence spread over the stone. On cooling and examining the diamond it was found that neither the colour nor the radio-activity had suffered appreciably.

The diamond is remarkable in another respect. It is extremely transparent to the Röntgen rays, whereas highly refracting glass, used in imitation diamonds, is almost perfectly opaque to the rays. I exposed for a few seconds over a photographic plate to the X rays the large Delhi diamond of a rose-pink colour weighing 31½ carats, a black diamond weighing 23 carats, and a glass imitation of the pink diamond. On development, the impression where the diamond obscured the rays was found to be strong, showing that most rays passed through, while the glass was practically opaque. By this means imitation diamonds can readily be distinguished from true gems.

I have already signified that there are various degrees of refractoriness to chemical reagents among the different forms of graphite. Some dissolve in strong nitric acid; other forms of graphite require a mixture of highly concentrated nitric acid and potassium chlorate to attack them, and even with this intensely powerful agent some graphites resist longer than others. M. Moissan has shown that the power of resistance to nitric acid and potassium chlorate is in proportion to the temperature at which the graphite was formed, and with tolerable certainty we can estimate this

temperature by the resistance of the specimen of graphite to this reagent.

The superficial dark coating on a diamond after exposure to molecular bombardment I have proved to be graphite (CHEMICAL NEWS, vol. lxxiv., p. 39, July, 1896). M. Moissan has shown that this graphite, on account of its great resistance to oxidising reagents, cannot have been formed at a lower temperature than 3600° C. (*Comptes Rendus*, cxxiv., p. 653).

It is thus manifest that the bombarding electrons endowed with an electric charge, and striking the diamond with enormous velocity, raise the superficial layer to the temperature of the electric arc, and turn it into graphite, whilst the mass of diamond and its conductivity to heat are sufficient to keep down the general temperature to such a point that the tube appears scarcely more than warm to the touch.

A similar action occurs with silver, the superficial layers of which can be raised to a red heat without the whole mass becoming more than warm (*Proc. Roy. Soc.*, vol. 1, p. 99, June, 1891).

I will now draw your attention to a strange property of the diamond, which at first sight might seem to discount the great permanence and unalterability of this stone. It has been ascertained that the cause of phosphorescence is in some way connected with the hammering of the electrons, violently driven from the negative pole, on to the surface of the body under examination, and so great is the energy of the bombardment, that impinging on a piece of platinum or even iridium, the metal will actually melt. When the diamond is thus bombarded in a radiant matter tube the result is startling. It not only phosphoresces, but assumes a brown colour, and when the action is long continued becomes almost black.

I will project a diamond on the screen and bombard it with radiant matter before your eyes. I do not like to anticipate a failure, but I am at the mercy of my diamond. I cannot rehearse this experiment, and it may happen that the diamond I have selected will show caprice and not blacken in reasonable time. Some diamonds visibly darken in a few minutes, while others, more leisurely in their ways, require an hour.

This blackening is only superficial, but no ordinary means of cleaning will remove the discolouration. Ordinary oxidising reagents have little or no effect in restoring the colour. The black stain on the diamond is due to a form of graphite which is resistant to oxidation.

Conversion of Diamond into Graphite.

Although we cannot convert graphite into diamond, we can change the diamond into graphite. I take a clear crystal of diamond and place it between two carbon poles, and throw the image on the screen by means of a powerful arc lamp behind. I now bring the poles with intervening diamond together and form an arc between. The temperature of the diamond rapidly rises, and when it approaches 3600° C., the vaporising point of carbon, it breaks down, swells, and changes into black and valueless graphite. I show this experiment because it is striking and suggestive. I may add that it is costly—because the stone if not of fine quality might easily burst.

And now with this risky experiment my Address draws to a close. I hope I have given you some idea of the underground wonders of the Kimberley mines; my two visits have opened my own eyes. I have tried to picture the strenuous toil of the men who bring to the surface the buried treasures; and I have given you some idea of the skill and ingenuity with which their labours are controlled. I have also given you a sketch of the fiery origin of the diamond, of the glowing, molten, subterranean furnaces where they first take shape. I have shown you that a diamond is the outcome of a series of titanic convulsions, and that these precious gems undergo cycles of strange and potent vicissitudes before they can blaze on a ring or a tiara.

As to myself, I am glad we have made this second journey. I shall always recall with interest the dusky smiling natives at work and at play. And I am glad to have seen that Arabian Nights vision, the strong-room of the De Beers Company, literally heaped with stones ardously won from the blue ground, purified, flashing, and of inestimable price. And, above all, I have vividly graven on my heart the friendly welcome, the innumerable acts of kindness, shown us by our able, energetic, and enterprising Colonial fellow countrymen.

EXAMINATION OF THE COMPARATIVE ABSORPTION OF HYDROGEN BY RHODIUM AND PALLADIUM.

By L. QUENNESSEN.

DURING the course of some researches on metals of the so-called platinum group, I had occasion to check certain properties mentioned by earlier writers.

Thus, according to Th. Wilm (*Berichte*, vol. xiv., p. 629), pure rhodium possesses a capacity for absorbing hydrogen much greater than that of palladium, and this statement is to this day repeated in various text-books. Further, Wilm stated that this property of absorption varies with the method adopted for the preparation of the metal; for example, rhodium obtained by the calcination of the double chloro-ammoniated salt had a greater absorbent power than the metal obtained from the double chloride of sodium or potassium, and that this absorption appeared to be due to a chemical affinity for the metal for hydrogen.

The solution of hydrogen in palladium having been examined by numerous chemists, my object has not been to approach this subject from the physical point of view, but only to compare the absorptive powers of rhodium and palladium for this gas. Now, my experiments in no way confirm those of Wilm.

Rhodium mixed with fused pulverised chloride of sodium was attacked by a current of chlorine at 440°, then, to eliminate the impurities which it might still contain, the product, taken up with pure water, was transformed into the double nitrite of rhodium and sodium (Joly and Leidié, *Comptes Rendus*, vol. cxii., p. 1259). This latter salt was divided into two portions; one treated with hydrochloric acid was brought to the state of double chloride of rhodium and sodium; the other portion was transformed to the state of double chloride of rhodium and ammonium, which was obtained perfectly pure by treating the double nitrite of sodium with chloride of ammonium to form the double ammoniacal nitrite, and then treating this nitrite with hydrochloric acid.

These two compounds were then heated and reduced at a dull red heat in a current of pure dry hydrogen, in which the rhodium sponge was allowed to cool.

In the case of the double salt of sodium we must take care, further, to remove the common salt by washing with warm water, and then repeat the treatment with hydrogen under the same conditions.

If, after complete cooling, we open the tube containing the boat full of rhodium, we observe the formation of water-vapour which condenses on the glass as soon as the metal comes in contact with the air; while if we drive off the atmosphere of hydrogen by means of a current of pure dry carbonic acid, the phenomenon of the formation of water on contact with the air is not produced. Further, if we place the boat of rhodium *in vacuo* and heat to 440°, by the use of a sulphur bottle, the barometer connected to the apparatus shows no variation of pressure, and it is quite impossible to extract the smallest bubble of gas with a mercury pump.

Further, it does not appear that the rhodium obtained from the decomposition of the chloro-ammonia salt has much more active properties than that obtained by the decom-

position of the chloro-soda salt, when this latter has been freed by levigation from the alkaline chloride surrounding it (L. Quennessen, *Comptes Rendus*, vol. cxxxix., p. 795).

On the other hand, pure palladium dissolved in dilute aqua regia was precipitated by chloride of ammonia, and the chloropalladate of ammonium obtained was dried and reduced at a dull red heat by pure dry hydrogen in the same manner as the rhodium salt.

If we let the palladium sponge cool in the current of hydrogen, and then afterwards allow the air to enter the tube containing the metal, we observe the formation of water-vapour which condenses on the sides of the glass.

Under these conditions the phenomenon has been identical up to the present with that observed with rhodium; but if we re-heat and again cool the palladium sponge under the same conditions, and then first drive out the atmosphere of hydrogen by means of a current of pure dry carbonic acid before allowing the air to enter, we again observe on opening the tube an abundant condensation of water-vapour on the glass; as we have already shown, this does not take place in the case of rhodium.

I have even confirmed this production of water immediately on contact of the air with palladium after continuing the current of carbonic gas for an hour and a-half.

These experiments, repeated several times, always gave the same results; we are thus entitled to state that rhodium does not resemble palladium in so far as the chemical affinity for hydrogen is concerned, but that it acts in the same manner as platinum sponge, condensing hydrogen and oxygen to form water.—*Bull. Soc. Chim.*, Series 3, vol. xxxiii., No. 3.

THE ACIDITY OF FRUITS.

By W. F. SUTHERST, Ph.D., F.I.C.

THE apparent increase of acidity in fruits after boiling will have been noticed by most people, the comparative sweetness of raw black currants, for instance, being changed to a mass of rather sour nature after cooking, necessitating the use of considerable quantities of sugar to render it palatable. To see whether acid were possibly formed in the process of boiling, a portion of a mixture of nearly ripe gooseberries and water was boiled for about thirty minutes and titrated with N/1 NaOH. The boiled portion, however, contained less acid than the raw berries, due, no doubt, to the volatility of some of the acids. The next point considered was whether the sugar was inverted or not during boiling. An unboiled quantity of gooseberries contained:—

Cane-sugar	1.16 per cent
Invert sugar	5.84 "

After boiling the mass contained:—

Cane-sugar	0.0 per cent
Invert sugar	6.91 "

Showing that all the sugar undergoes inversion during cooking, the acid present bringing this about as in the usual process of hydrolysis. One other thing noticed in eating raw fruits is that the pulp only is eaten, especially in such fruits as plums, gooseberries, currants, &c., and when the skin and pulp of gooseberries were analysed for acidity they showed the following:—

Skin	2.66 per cent (expressed as tartaric acid)
Pulp	1.80 " " "

Now, of course, during the boiling or cooking of fruits, the whole of the acid in the skin is extracted and the semi-liquid mass therefore contains all the acid evenly distributed, whilst if the fruit is eaten raw, and the skin not masticated this extra acidity is not tasted. This latter experiment, perhaps, shows how this phenomenon is brought about.

The Agricultural College, Tamworth.

THE
REDUCTION OF ZIRCONIA WITH MAGNESIUM
AND THE SPONTANEOUS FORMATION OF
ZIRCONIUM NITRIDE.

By E. WEDEKIND.

ZIRCONIUM is one of those elements whose preparation in the pure state presents great difficulties. Of the three allotropic modifications* in which zirconium is said to occur, the crystallised has been the most thoroughly investigated, while the amorphous element has not been further examined since the experiments of Berzelius and Troost; in particular, the conversion of amorphous zirconium into the compact or crystalline modification has not been performed. I hope to be able to report shortly on experiments on this point; the subject of this communication is the reduction of zirconium dioxide by magnesium and aluminium. According to the statements of T. L. Phipson (*cf. Comptes Rendus*, lxi., 745) and the experiments, more recently performed, of Dennis and Spencer (*Journ. Am. Chem. Soc.*, xviii., 673) it must be possible to obtain by the action of magnesium on the oxide, amorphous zirconium, the preparation of which from zirconium potassium fluoride by Berzelius's method is uncertain and inconvenient. Clemens Winkler (*Berichte*, 1891, xxiv., 888; and xxiii., 2664) by heating (two atoms of) magnesium with (one molecule of) zirconium dioxide in a current of hydrogen obtained only a mixture of zirconium hydride, ZrH_2 , and unchanged zirconia; but it was not thereby proved to be impossible that, in the absence of hydrogen, and on using an excess of magnesium and applying a higher temperature, the reaction would proceed as desired according to the equation $ZrO_2 + 2Mg = Zr + 2MgO$.

After the reduction of metallic oxides by means of aluminium according to Goldschmidt's method had rendered possible the preparation of several difficultly fusible metals in the compact condition, an attempt was made to convert the oxide into the free element by the aid of aluminium. It was then found that an intimate mixture of zirconia and aluminium—both granular and powdered metal were used—generally reacted with difficulty and incompletely, the reaction not spreading throughout the whole mass. In some experiments—especially when small quantities were used—a grey mass was obtained which contained relatively little unchanged oxide, but the rise of temperature was in no case sufficient to fuse the elements set free, and thus to render possible its separation from the aluminium oxide simultaneously formed. The product of the reaction, which was freed from excess of aluminium by treating it with dilute acids, consisted of a green crystalline powder, from which, however, the alumina could not be removed on account of its insolubility in acids and alkalis. As the powder, even when strongly compressed, does not conduct the electric current at all, it was impossible to fuse the material and thus purify it with the aid of its own resistance by the method described by me for aluminium zirconide (*cf. E. Wedekind, Zeitschr. f. Elektrochem.*, 1904, 332); nor had heating in the electric furnace had any effect. Thus I was obliged to fall back upon the old method of reducing with magnesium.

According to Phipson (*loc. cit.*, and *Journ. Prakt. Chem.*, [1], xcvi., 448) the reduction of zirconia, which is said to proceed as easily as that of silicic and boric acids, occurs at the moment of the fusing of the magnesium, and the zirconium is obtained in the form of a velvety black powder, from which the magnesia formed is removed by means of dilute hydrochloric acid. No analytical data are given to show that Phipson really had obtained pure elementary zirconium. Dennis and Spencer (*loc. cit.*) worked in an atmosphere of hydrogen, using Winkler's method, with

this modification, that heating in the current of hydrogen was repeated till reduction was as nearly as possible complete. The product contained 80.7 per cent zirconium and 18 per cent oxygen (the residue consisted of small quantities of silicon, magnesium, and hydrogen). Dennis and Spencer are of the opinion that the product of their reaction contained only a little elementary zirconium, and consisted chiefly of zirconium monoxide, ZrO .

I performed the reduction of zirconia as follows:—

The bottom of a crucible* of pure nickel, of height 11 c.m. and diameter 4 c.m., was covered with a thin layer of magnesium powder, upon which was placed an intimate mixture of zirconium dioxide and magnesium powder (40 per cent more than the calculated quantity), and pressed down with a pestle. Magnesium powder was then scattered over the whole. The quantity of the reaction mixture was so measured that the crucible was only one-third filled; it was then covered with a well-fitting cover, and heated before a good blowpipe till the lower part became red-hot; the commencement of the reaction is revealed by hissing, and sometimes the lid is hurled off. At this moment the blowpipe flame is drawn away; the crucible glows for some time longer owing to the heat of the reaction.† After cooling a brownish black powder is obtained, which cakes together and smells distinctly of ammonia; this was then rubbed up under water, and digested at a gentle heat with concentrated ammonium chloride solution in order to remove the excess of magnesium. When the evolution of gas had ceased, warm dilute hydrochloric acid was added till a faintly acid reaction was obtained. After the dark powder had settled, it was twice decanted, filtered, and washed with water; at a definite point in the washing process a part of the product went colloiddally through the filter; the solution was dark blue in transmitted light and greyish opalescent in incident light. It may be mentioned that in a few experiments for some unexplained reason, a colloidal solution of grey-brown colour was obtained. In all cases after repeated washing the colloidal substance in the precipitate was visibly removed; the filtrate ran through perfectly clear; but I noticed that the residue on the filter, the quantity of which had not appreciably diminished, could again be made to yield a colloidal solution, by treating it with warm dilute hydrochloric acid and then washing with cold water; at a definite stage the earlier effect again appeared. If after washing a few times the filtrate again ran through colourless, the process could be repeated. Thus this was a periodic phenomenon, something like Ostwald's solution of chromium in acids. The united colloidal solutions—blue as well as greyish brown—and the residue on the filter were examined separately.

The Colloidal Product Soluble in Water.

The fact that one part of the product of the reduction of zirconia goes into solution in the colloidal form was of importance to me, for I hoped I should be able to obtain thus zirconium, which is difficult to obtain pure, for insoluble compounds—especially unchanged oxide—must remain behind in the residue on the filter. It was therefore a question of precipitating the dissolved substance again in a suitable form, and characterising the gel thus obtained as elementary zirconium. But all my efforts in this direction, in spite of many attempts, were fruitless, chiefly because the concentration of the solutions was only exceedingly small, and hence only very little material could be procured. Moreover, it was found that the colloidal solutions‡ could not be made to yield flakes so readily as other colloidal solutions; electrolytes, such as sodium chloride, ammonium chloride, and hydrochloric acid, produce no effect; however, on boiling with hydrochloric acid a turbidity appeared; the fine precipitate thus obtained shows a

* The third modification is the graphitic, described by Troost; this is said to result on the decomposition of the compound of zirconia with caustic soda by means of iron, at the temperature of the melting-point of copper; this statement requires confirmation, all the more because iron is a less powerful reducing agent than aluminium or magnesium.

† Nickel crucibles of the form described were supplied to me by the Vereinigte Deutsche Nickel Werke in Schwerte. Clay crucibles cannot, of course, be used on account of the presence of magnesium.

‡ In most cases some part of the nickel crucible fuses.

§ The stability of the solutions varies; most of them after a time deposit a precipitate which does not apparently increase. Also in dialysis experiments flakes were observed clinging to the porous wall.

tendency to go into solution again after being filtered off. A fairly trustworthy precipitant was found in hydrogen peroxide, this being apparently not decomposed by the colloidal substance. On addition of hydrogen peroxide, flakes were slowly formed; the blackish precipitate, which shows a greenish sheen on the surface, may be filtered, but it is difficult to wash it, as it fills up the pores of the filter; fixed alkalis also produce a precipitate. The difficulties of obtaining a preparation sufficiently pure for analysis could not be overcome. A gel, precipitated by hydrochloric acid and afterwards dried in the desiccator and at 100°, was converted into colourless zirconium dioxide by heating in a platinum crucible:—

0.326 grm. of the substance gave 0.3429 grm. ZrO_2 (pure elementary zirconium would have yielded 0.4499 grm. of oxide).

A preparation precipitated with hydrogen peroxide behaved similarly:—

0.4487 grm. of the substance gave 0.44935 grm. of ZrO_2 .

Many preparations could not be brought to constant weight, as the moisture in the gel did not escape completely at the temperature in question. When such a preparation was heated *in vacuo*, on the cold part of the tube it was possible to see not only a deposit of moisture, but also a yellowish white sublimate. A specimen of a preparation thus treated gave on ignition not an increase but a small decrease of weight:—

0.2281 grm. of the substance gave 0.2194 grm. ZrO_2 .

The chemical nature of the colloiddally dissolved substance could not be established; from its behaviour on being heated in rarefied air it was probably an adsorption compound of zirconium or zirconium nitride with zirconium oxychloride,* and it seems probable that the grey-brown colloid is zirconium itself, as Berzelius (*cf. Pogg. Ann. d. Phys. u. Chem.*, 1825, iv., 121) has already observed that his amorphous zirconium gave in pure water a dark brown colour, which appeared dark grey in reflected light. The blue colloid might then be regarded as the absorption compound of zirconium nitride (see below).

The colloidal nature of the solution in question was proved by its behaviour under the electrical potential gradient; for this purpose a U-shaped glass tube was used, platinum discs of about 10 m.m. diameter being employed as electrodes;† a sensitive ampere meter and potentials of 24–104 volts were also used. Although the solutions were rendered faintly acid with hydrochloric acid, the conductivity was small, as the following table shows:—

Grey-brown Colloid.‡

Potential, in volts.	No. of mill.-amps.	Resistance, in ohms.
24	4	6000
68	13	5200
104	14	7400
104	17	6100

The phenomena observed were the same with all potentials; the cathode was soon covered with a fine black deposit, and had the appearance of a platinised electrode; in the neighbourhood of the cathode the flakes were thickest. When the current was commuted the strength of the current rose for a moment to 24 mill.-amps. The electrode covered with the black deposit soon became clean again, while the other one blackened. The flaking was only incomplete. On using a very dilute perfectly transparent solution the formation of black clouds could be plainly observed; these migrated to the cathode. No sudden flaking took place. In this case with a potential of 104 volts 4 mill.-amps. went through the liquid, corresponding to a resistance of 26,000 ohms. The electrolysis was in all cases very feeble.

* This is confirmed by the coagulation by alkalis, which decompose the oxychloride, when the colloid is brought down.

† The electrodes were about 6.5 c.m. apart.

‡ The blue colloid behaves perfectly analogously.

The dissolved particles thus migrate to the cathode; this discovery was surprising, because Whitney at the meeting of Section X. of the International Congress for Applied Chemistry (Berlin, 1903) had reported (*cf. Zeit. f. Elektrochem.*, 1903, ix., 633) that colloidal zirconium under the influence of an electric potential gradient migrates in the direction of the negative current, like colloidal platinum and many other simple substances. As Whitney had given no information about the preparation of this colloidal zirconium, I asked for a private communication on the subject. Mr. J. E. Ober, Prof. Whitney's collaborator, was then kind enough to place the information at my disposal. The material used for the experiments was prepared by the action of magnesium on zirconium tetrachloride, and purified in the same way as my reduction product, but a perfectly neutral solution of the colloid was obtained, otherwise resembling my (blue) preparation. The transport experiments were so arranged that electrolytic products of decomposition could not reach the colloid; the latter was attracted by the positive electrode. There was no analytical proof of the elementary nature of the colloidal substance. Ober also investigated the reduction of zirconia with magnesium, and the product obtained by him corresponds approximately to the composition of a suboxide, ZrO , as well as the black colloid obtained at the same time. It is clear that the question of the nature of the colloidal reduction products of zirconium dioxide with magnesium presents greater complications than was to be expected, and requires further investigation.*

Finally, as regards the cause of the periodic phenomenon on the formation of the colloidal reduction product (see above) I am inclined to agree with an opinion expressed by G. Bredig, namely, that when magnesium acts upon zirconia, first an alloy or compound of zirconium with magnesium is formed, and is then destroyed by acids, when the zirconium or the nitride remains behind in the colloidal state (*cf. Zeit. f. Elektrochem.*, 1903, ix., 631; Discussion on the lecture "Colloidal Zirconium," in Section X of the International Congress for Applied Chemistry, 1903). If we assume that this process is stopped in consequence of partial inclusion of the alloy in insoluble substance, and is set going again by contact with fresh acid, the periodicity of the process would be explicable up to a certain stage.† Such periodic phenomena have been occasionally observed in electrolytic processes, e.g., in the electrolysis of sodium carbonate with mercury electrodes according to Arrhenius (*Zeit. Phys. Chem.*, 1893, xi., 805); also with lead at high current densities, and with lead-sodium if it is chemically attacked (*cf. Bredig and Haber, Berichte*, 1898, xxxi., 2741; Haber and Sack, *Zeit. f. Elektrochem.*, 1902, viii., 251; M. Reuter, *Ibid.*, viii., 801; and Sack, *Zeit. Anorg. Chem.*, 1903, xxxiv., 286).

In agreement with observations from other sources (*cf.*, among others, E. Jordis and E. H. Kanter, *Zeit. Anorg. Chem.*, 1903, xxxv., 21) it appears that in the case described certain small impurities—chiefly zirconium oxychloride (see above) and perhaps some zirconium hydride—favour or even render possible the formation of the colloidal substance.

The Insoluble Residue (Zirconium Nitride).

The residue remaining on the filter after washing the colloid forms a brownish green crystalline powder, which appears under the microscope like a magma of bronze-coloured small crystals with a faint greenish surface sheen. On gently heating‡ in the air it forms colourless zirconia,

* The fact that the dissolved particles in the solutions obtained by me migrate to the cathode and are thus positively charged, seems to me to argue against their elementary nature, for most colloidal elementary substances migrate in the direction of the negative current.

† As the substance was well rubbed up before the treatment with hydrochloric acid, it was to be expected *a priori* that any magnesium zirconide present would be completely decomposed by the excess of acid employed.

‡ The nitride burns with glittering sparks on being sprinkled in a flame.

but is otherwise of remarkable stability both towards acids—with the exception of hydrofluoric acid—and towards alkalis; even when it is boiled for some time with the latter no ammonia is evolved. If, however, the substance is introduced into fused caustic alkali, when a feeble luminescence phenomenon is to be observed the presence of nitrogen is revealed by a distinct ammonia reaction. The combined nitrogen may also be demonstrated as such if the nitride is oxidised in an atmosphere of carbon dioxide, and the nitrogen thus set free is collected. For this purpose weighed quantities of the substance were mixed with fine granular copper oxide, and, as in nitrogen determinations in the case of organic substances, burnt in a tube of difficultly fusible glass containing a reduced copper spiral; the gas evolved was collected in an azotometer over caustic potash, and measured:—

- I. 0.4025 grm. of the substance gave 31 c.c. of nitrogen at 20° and 731 m.m. pressure, corresponding to 8.47 per cent N.
- II. 0.5553 grm. of the substance gave 41 c.c. of nitrogen at 16° and 743 m.m. pressure, corresponding to 8.3 per cent N.

An attempt to determine the nitrogen in the potash melt quantitatively as ammonia failed, owing to experimental difficulties.* The increase of weight on converting it into zirconium dioxide was therefore determined. A specimen of the raw product gave the following number:—

- 0.8819 grm. of the substance gave, after ignition to constant weight, 0.8972 grm. ZrO_2 (increase of weight, 0.0153 grm.). A preparation purified by washing with bromoform gave a number agreeing with the theory for the nitride, Zr_2N_3 .
- 0.8752 grm. of the substance gave 0.9632 grm. ZrO_2 (observed increase of weight, 0.088 grm.; calculated for Zr_2N_3 , 0.086 grm.). Calculated for Zr_2N_3 : Zr, 81.2; found Zr, 81.35.

Matthews (*cf. Journ. Am. Chem. Soc.*, 1898, xx., 843) prepared two zirconium nitrides, Zr_2N_8 and Zr_2N_3 , by another method—by heating zirconium chloride ammonia; the product obtained by me from zirconia appears to consist essentially of the nitride, Zr_2N_3 . In order to see whether the difference in the nitrogen result is due to the presence of unchanged zirconium oxide, in another experiment the latter was determined by dissolving the substance in concentrated hydrofluoric acid, collecting the insoluble residue on a small filter,† and igniting. The filtrate was evaporated to dryness, moistened with concentrated sulphuric acid, and ignited to constant weight. 0.3868 grm. of the substance left an insoluble residue of 0.0156 grm. ZrO_2 , and gave, after conversion into the oxide, 0.4105 grm. ZrO_2 .

The preparation in question therefore contains 3.52 per cent unchanged or regenerated zirconium dioxide; after subtracting this the zirconium percentage works out to 81.31 per cent. (Theoretical amount for Zr_2N_3 , 81.2 per cent Zr).

The amount of zirconia is thus not great enough to explain the deficiency of nitrogen. We are therefore forced to conclude that the zirconium nitride mixed with the copper oxide is only incompletely burnt on heating in an atmosphere of carbon dioxide. As a matter of fact, in the potash melt a portion of the substance remains dark coloured, and thus seems to escape decomposition.

The zirconium nitride resulting on the reduction of zirconia in the air is attacked readily, not only by oxygen, but also by chlorine, forming zirconium tetrachloride at a faint red heat. The yield is certainly not satisfactory, but at any rate we have here a method of quickly and conveniently preparing small quantities of this chloride, which is otherwise not easily obtained. The nitride becomes luminescent on being heated with bromine vapour, and the

preparation of zirconium tetrabromide—especially on the small scale—is thus performed very simply: zirconium oxide is first converted into the nitride as described above, and the latter, on being heated with bromine in a test-tube, gives a crystalline sublimate of zirconium bromide, fuming in the air.

The nitride is remarkably stable towards concentrated nitric acid, even on heating, and also towards aqua regia. In the form of a pressed powder, the compound does not conduct the electric current.*

The tendency to form zirconium nitride must be fairly great, for even by acting with magnesium on zirconia in a rarefied space—using an iron tube—a crystalline powder is obtained; this powder, on oxidation, exhibits only a slight increase of weight. Since, when aluminium is used, the formation of zirconium nitride decreases very much, it must be supposed that the magnesium nitride first resulting from the excess of magnesium† functions as a nitrogen carrier, and promotes the formation of zirconium nitride.

Finally, it must be emphasised that no support has been found for the existence of a divalent zirconium compound—the long-sought zirconium monoxide, ZrO . In agreement with the experimental results of Cl. Winkler, it has been found that zirconia cannot be completely reduced by magnesium. Moreover, it appears that the nitrogen of the air readily takes a direct or indirect part in the reaction, and causes the formation of the difficultly saponified but easily oxidised zirconium nitride. The statement of Phipson (see above), who claims to have obtained elementary zirconium by the action of magnesium on zirconia, cannot be checked, owing to the lack of further information and analytical data, but most probably Phipson had obtained only zirconium nitride or a mixture of it with zirconium.—*Zeit. Anorg. Chem.*, 1905, xlv., 385.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES. General Monthly Meeting, July 5th, 1905.

H. A. LENEHAN, F.R.A.S., President, in the Chair.

MR. W. A. DIXON, by permission of the President, made the following remarks:—

He had often found that young men were quite willing to work out any investigation, but that they were not aware of any subject which would repay them; he therefore desired to suggest one in which he had found no information. He thought it deserved investigation, but had no time himself to attempt it. He had in his dining-room a Fletcher's gas-fire, an upright fire-clay block, with tufts of asbestos heated to radiation of heat point by a Bunsen flame. Some years ago, sitting in front of this, it occurred to him that it would be an improvement to convert the colourless flame to a coloured one, and therefore twisted some wires into a rope and saturated this with brine to obtain a sodium flame. Next night, the fire having got hot, he introduced the saturated wire at the base of the flames, and immediately found a great reduction in the radiation, so that he felt quite cool. Removal of the wires and re-insertion several times always produced the same effect.

The subject he had to suggest was, therefore, "The radiation from coloured flames." To this might very well be added the absorption of radiant heat by coloured glass, which varies much. In this part it would be necessary to

* The filament of the new zirconium lamp (D.R.P. 133701 and 137569) consists of a mixture of compounds of zirconium with nitrogen, hydrogen, and carbon, to which rhodium is also added in order to obtain the necessary conductivity.

† On using the calculated quantity of magnesium, in one experiment a grey crystalline powder was obtained, which did not appear to be identical with the zirconium nitride investigated.

* Complete decomposition requires temperatures which the material of the vessel will not stand.

† Ignited zirconium oxide is practically insoluble in hydrofluoric acid.

use coloured glass of standard light penetration, such as is used in Lovibond's tintometer.

Remarks were made by Dr. F. H. Quaife and Mr. G. H. Knibbs.

The following paper was read:—

"*Observations on the Illustrations of the Banks and Solander Plants.*" By J. H. MAIDEN, Government Botanist, and Director of the Botanic Gardens, Sydney.

The issue of the third and final volume and plates, from the coppers engraved in the Eighteenth Century from drawings by Nodder, Cheveley, and the two Millers, prepared under the direction of Banks, and depicting over 400 plants collected by him in 1770 during Cook's first voyage, is—to Australians at least—an important historical event, which assuredly demands the most marked emphasis that Australians can give it.

The present work has been written by Mr. James Britten, of the British Museum, with the authority of the trustees of that institution. Many of Banks' plants depicted were presented by the trustees to the National Herbarium, Sydney. The scope of this work is explained, and the proposed changes in nomenclature are indicated and compared with the names in the "Flora Australiensis."

This handsome publication, apart from its historical value, is a notable addition to existing iconographies of Australian plants.

Remarks were made by Messrs. W. J. Clunies Ross, R. T. Baker, W. M. Hamlet, and the author.

General Monthly Meeting, August 2nd, 1905.

The following paper was read:—

"*The Refractive Indices, with other Data, of the Oils of 118 Species of Eucalyptus.*" By HENRY G. SMITH, F.C.S., Assistant Curator, Technological Museum, Sydney.

In this paper the author records the refractive index, the specific gravity, the specific refractive energy, and the solubility in alcohol of the oil of each species. The material was distilled at the Museum, and most of it had been prepared for the work "Research on the Eucalypts and their Essential Oils," by Mr. R. T. Baker and himself, so that it was of undoubted origin. The oils of those species which have been obtained since that work was published are also included. By working upon the oils of such a large number of species it was possible to arrange the results in some order. The specific refractive energy results cannot be used to any great extent for the purpose of classification, but if the refractive index be multiplied by 10 times the solubility in 70 per cent alcohol (sp. gr. 0.8722 at 15.5° C.) a very good arrangement of the eucalypt oils can be made. Those oils which contained eucalyptol in excess had, as a rule, the least refractive index, and were the most soluble in alcohol. As the pinene increased in amount the solubility diminished, and although the refractive index remained much the same, yet the resulting figures increased considerably. The solubilities were taken in tenths, and the temperature for all the determinations was 16° C. The oils of the 51 species in the eucalyptol group had refractive indices ranging from 1.4686 to 1.4774, and the solubility was from 1.05 to 8 volumes 70 per cent alcohol, down to No. 45, the remaining six being insoluble in 10 volumes. The specific gravities of the oils of this group were mostly above 0.91. The 7 pinene oils in which phellandrene was absent had refractive indices ranging from 1.4741 to 1.4788, and none were soluble in less than 7 volumes 80 per cent alcohol. The pinene oils (14 species) in which the sesquiterpene was pronounced, and phellandrene absent, had refractive indices ranging from 1.4801 to 1.4948, while the oils which contained the aldehyde aromadendral in some quantity, and in which phellandrene was absent (9 species), had refractive indices from 1.4828 to 1.4946. The refractive indices of the phellandrene oils which contained piperitone (11 species) ranged from 1.4828 to 1.4945. The 22 phellandrene oils in which the sesquiterpene was

a pronounced constituent had refractive indices ranging from 1.4801 to 1.5065. The perfumery oils, as *E. citriodora*, *E. macarthurii*, and *E. Staigeriana*, were not classified.

Remarks were made by Mr. W. A. Dixon, Mr. W. M. Hamlet, Dr. George Harker, and Mr. G. H. Knibbs. The author replied.

NOTICES OF BOOKS

The Synthetic Dye-stuffs and the Intermediate Products from which they are Derived. By JOHN CANNELL CAIN, D.Sc. (Manchester and Tübingen), and JOCELYN FIELD THORPE, Ph.D. (Heidelberg). London: Charles Griffin and Company, Ltd. 1905.

THIS work will probably soon be regarded as invaluable both by technical students and by dye-works chemists. It is exceedingly practical, and possesses the great advantage of advocating the use of only such reagents as would in all probability be found in a works laboratory, and, moreover, it describes only those quick and simple methods which are actually the best to be employed technically, and not those which are of scientific interest only. The book is divided into three parts. The first gives theoretical descriptions of the various intermediate products and dye-stuffs, and shows very clearly the structure, reactions, and transformations of the various classes of dyes. The second part describes the methods of preparation of the more important intermediate products and dye-stuffs, concise directions being given for their preparation on the small scale, and short notes on such of their properties as the student should investigate for himself experimentally, while the last part details the methods of identification of the same substances, the valuation of colouring matters and their application, and in fact all that is likely to be required of a chemist in the way of analytical investigation. The importance of a thorough knowledge of the theory of dyeing is rightly emphasised, and every facility is given for the student to acquire such knowledge and to enable him to apply it intelligently in practice. It is difficult to see how the plan the authors have adopted could be improved upon, and no better book could be recommended, more especially for the use of technical students.

Premature Burial and How it may be Prevented. By WILLIAM TEBB, F.R.G.S., and COL. EDWARD PERRY VOLLUM, M.D. London: Swan Sonnenschein and Co., Ltd. 1905.

THE second edition of this work has been slightly enlarged and brought up to date by Dr. Walter R. Hadwen, who has added new cases of importance to the gruesome list which the original authors had compiled and annotated. According to the authors a certain amount of reticence has been shown in not including the most horrible cases on record, and for this they are much to be commended; in so doing they have not weakened their case in favour of legislation in the way of altering the present law as regards the delay of burial till the one unmistakable sign of death has ensued, the giving of death certificates, and the provision of waiting mortuaries similar to those already in use on the Continent.

Die Elektrolytische Chloratindustrie. ("The Electrolytic Chlorate Industry"). By JOHN B. C. KERSHAW, F.I.C. Halle-a-S.: Wilhelm Knapp. 1905.

THE author of this monograph, which forms the nineteenth volume of the series of monographs of applied electrochemistry, has had many difficulties to contend with in collecting his material, the chief being due to the unwillingness of manufacturers to give details of the works under their control. This secrecy is always a marked feature of the beginnings of an industry, and in this case it accounts for the lack of information regarding plant and cost of working to be found in the book. However, the author has done his utmost with the material at his disposal, and

has produced a very useful monograph. He outlines the growth of the industry from its earliest beginning, and as he is of the opinion that it is best to study thoroughly the work of the earlier investigators, he includes descriptions of processes which may now be regarded as superseded. While this plan of tracing the development of the industry undoubtedly leads to the production of a most interesting work, it appears doubtful whether it is altogether advisable when the space at the disposal of the author is limited, and it would probably be best to follow the mean course between this plan and that of neglecting all early work altogether. The book has been ably translated into German by Dr. Max Huth.

La Chimie Minérale, Ses Relations avec les Autres Sciences. ("Mineral Chemistry and its Relations to the other Sciences"). By HENRI MOISSAN. Paris: G. Steinthal. 1904.

THIS lecture, delivered before the Congress of Arts and Sciences at the Exhibition at St. Louis in September, 1904, gives a short historical account of the developments of inorganic chemistry from the earliest times, and of the assistance it renders towards the solution of the problems of other sciences. As regards the fusion of physics and chemistry, the recent advances made by the aid of spectrum analysis, and of electrolytic processes and the production of high and low temperatures, all provide the author with subjects of which to give graphic accounts. He also discusses briefly the connections between biology, astronomy, mathematics, and geology and chemistry, the whole lecture being full of suggestion and most stimulating reading.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY EXAMINATIONS.

To the Editor of the Chemical News.

SIR,—I have read with much interest the article on the Scheme for Examinations in Technical Chemistry in connection with the Institute of Chemistry (CHEMICAL NEWS, vol. xcii., p. 155).

Some scheme of this nature is very much needed, but at the same time if the exact lines denoted in the article are strictly followed, a great number of works chemists will still be debarred from the advantages, because of Clause 2, which states that the "examinations will be open only to Fellows, and to those Associates who have been registered as such for at least one year."

There are many chemists employed in technological work who have never had the opportunities and advantages which are necessary to become A.I.C. or F.I.C.; that is, have not been able to attend colleges recognised by the Institute, &c., and still who could produce evidence of good general education, and Honours Certificates from the Board of Education in several subjects probably, relating more particularly to their own sphere of work.

In my opinion, the scope of usefulness of the proposed scheme would be much widened if an extra conditional clause be inserted therein to the effect that candidates satisfying certain conditions, based on some such considerations as the above, be admitted to the examinations in technical chemistry.

While dealing with this subject I may say that a kindred matter has often occupied my thoughts with regard to the Board of Education and City and Guilds of London certificates. A person holding Honours Certificates granted by these bodies has absolutely no "status" compared with a B.Sc., A.I.C., or F.I.C. Is it not time that this was remedied, and that some kind of degree or distinction be associated with these diplomas? Surely they are worth it.

In the hope that this letter may induce others to state their views on the subject, and ventilate the question generally, I am, &c.,

TECHNICUS.

VON KOBEL'S TEST FOR BISMUTH.

To the Editor of the Chemical News.

SIR,—In performing the test for bismuth known as Von Kobel's, it occurred to me to try whether any other metals gave similar results. I then found that arsenic and antimony both gave red sublimates when treated with this reagent on aluminium plate.

The arsenic reaction was quite as delicate as the bismuth, and the red was much lighter and faded off to a lemon-yellow. The antimony reaction was less delicate, and in quantity resembled the bismuth.

As these results do not appear in any of the standard works, perhaps some of your readers may be interested in them.—I am, &c.,

D. E. RAMSEY.

80, Elspeth Road, Clapham Common, S.W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 10, September 4, 1905.

Constitution of Copper-aluminium Alloys.—Leon Guillet.—The author's investigations on the subject of the copper-aluminium alloys show the presence of seven constituents:—1. A solution containing 0 to 8 per cent of aluminium; this constituent has often been confused with the constituent Cu_3Al . 2. The compound Cu_3Al or a solid solution of this. 3. A solid solution which is produced during tempering. 4. A solid solution in which the proportion of aluminium varies between 14 to 30 per cent. 5. The compound Al_2Cu . 6. A compound similar to Al_2Cu , but not quite identical. 7. Either pure aluminium or an aluminium-copper solution containing a very small proportion of copper. It is probable that there also exists a solution containing 44 to 46 per cent of aluminium.

MISCELLANEOUS.

New Zealand International Exhibition.—The Government of New Zealand has decided to hold an International Exhibition during the summer of 1906-7, at Christchurch, Canterbury, New Zealand, in which all nations of the world have been invited to participate. The object of the Exhibition is educational, and it is intended to demonstrate the resources and possibilities of the Colony as one of the world's food-producing factors, its vast mineral resources, and to draw attention to its unrivalled and varied scenery, thermal wonders, and the exceptional opportunities offered to sportsmen. It is further intended to bring under the notice of the more industrial nations of the world the great field the Colony of New Zealand offers as an outlet for enterprise, and for the use and consumption of all manner of up to date appliances, manufactures, &c. As a food-producing country it is only necessary to instance the rapid growth of the development of the New Zealand frozen meat industry, and the dairying industry, which is still only in its infancy. New Zealand's mineral wealth is shown by the continuous and increasing output of gold, which, in the past fifty years, has totalled £65,000,000 in value. There are also large deposits of coal, iron-sand, and iron-ore in the Colony. Further particulars may be obtained from the Secretary of the Local Committee Christchurch, New Zealand.

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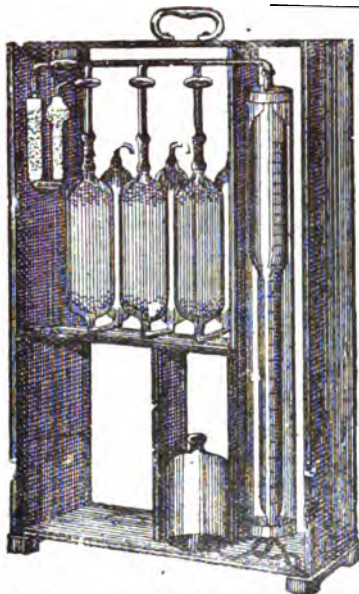
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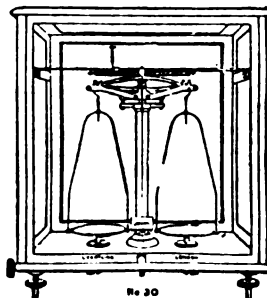
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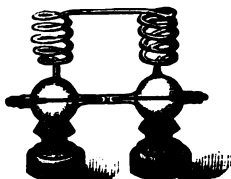
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In the CHEMICAL NEWS of June 2, 1905, pp. 253-4

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THE CHEMICAL NEWS.

VOL. XCII., No. 2394.

ON THE THERMO-ELECTRIC JUNCTION AS A MEANS OF DETERMINING THE LOWEST TEMPERATURES.*

By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S.

THE inconvenience of using the gas thermometer at very low temperatures and the failure of platinum and other metal resistance thermometers within 30° or 40° of the absolute zero, led me some years ago to consider the experimental behaviour of the thermo-electric junction at the lowest temperatures. My special object at the time the experiments were made was to have a further confirmation of the melting-point of hydrogen, and also of the lowest temperature reached on exhausting solid hydrogen, other than that I had found by means of the hydrogen gas thermometer ("The Boiling-point of Liquid Hydrogen, Determined by Hydrogen and Helium Gas Thermometers," *Proc. Roy. Soc.*, 1901, vol. lxviii.). The results have remained unpublished, because my intention has always been to extend them to other thermo-electric combinations. Not having been able to accomplish this project, they are now abstracted as affording useful information in this field of investigation, and as furnishing a general confirmation of my previous investigations.

A German-silver platinum couple was selected as likely to give the most uniform results at low temperatures, although subsequent experiments have led to the conclusion that it would have been better to have replaced the platinum by gold. As regards resistance thermometers, I have shown that gold is more reliable than platinum at temperatures near the boiling-point of hydrogen (Bakerian Lecture, "The Nadir of Temperature and Allied Problems," *Proc. Roy. Soc.*, 1901, lxviii.). The difficulties of the investigation were considerable; it had to be carried out at the time in the neighbourhood of the machinery producing the liquefied gases required in the investigation—namely, oxygen, nitrogen, and hydrogen—so that the zero of the delicate galvanometer employed did not remain quite constant. To remedy this I inserted a rocking make-and-break in order to get the readings of each observation at both ends of the scale. In the process of removing one difficulty another presented itself, through the development of small but appreciable thermo-electric currents in the rocker. Precautions had to be taken against these, and at all other metal junctions against similar small thermo-electric currents, and it was even found necessary to have a correction on account of the resistance box inserted in the circuit to bring large readings within the limits of the scale. The galvanometer and resistance box were inserted in the German-silver branch of the couple, the points of junction of the copper leads with the German-silver ends of the couple being insulated and placed close together within a vacuum test-tube packed with cotton-wool to ensure equality of temperature.

Preliminary experiments showed that the junctions altered after having been subjected to the temperature of liquid hydrogen. However, on resoldering the junctions with hard silver solder instead of soft solder, the thermo-couple accurately repeated observations at the temperature of liquid oxygen, after having passed through a liquid hydrogen bath. From this it appears that all such couples before calibration ought to be cooled suddenly in liquid air and then rapidly heated to the ordinary temperature, a similar operation being repeated with liquid hydrogen. If the couples return to their original state after such abrupt changes of temperature, then they are in a fit state for calibration.

Three series of observations were made to determine whether the resistance of the junctions varied to a noticeable extent with the temperature, namely, at the freezing-point of water, at the boiling-point of oxygen, and at the boiling-point of hydrogen. Six very concordant observations with varying resistances in the resistance box were made between 0° C. and 15° C. These were reduced by the method of least squares, and gave for the resistance of the circuit 3,500 ohms. Five similar results between the melting-point of nitrogen and the boiling-point of oxygen gave, by least squares, 3,293 ohms. Only two observations were taken in liquid hydrogen, which are therefore not entitled to the same weight as those already given, but the resistance appeared again about $3\cdot3$ ohms. As the variation of the resistance of the circuit was so slight, an attempt was made to reduce the results on the assumption of constancy, but this was not satisfactory. However, on treating the variation of the resistance of the circuit as linear with the temperature, the data came into better agreement.

Table I. contains the details of the observations made with the silver soldered German-silver platinum couple, the recorded readings of the galvanometer being the means of several observed readings, corrected when necessary for resistance introduced into the circuit.

TABLE I.

No. expt.	Substances used for difference of temperature.	Corresponding absolute temperatures.	Mean absolute temperature.	Mean galvanometer reading.	dE/dt .
1.	Water at 15° and ice	$280^{\circ}, 273^{\circ}$	$280^{\circ}5$	463.2	$30^{\circ}88$
2.	Boiling carbonic acid and ethylene	195, 170	182.5	693.5	$27^{\circ}74$
3.	Boiling ethylene at 10 m.m. and oxygen	$123^{\circ}5, 90^{\circ}5$	107	724.0	$21^{\circ}94$
4.	Boiling oxygen and nitrogen ..	$90^{\circ}5, 77^{\circ}5$	84	279.0	$21^{\circ}46$
5.	Boiling nitrogen and melting nitrogen	$77^{\circ}5, 62^{\circ}5$	70	320.7	$21^{\circ}38$
6.	Boiling hydrogen and melting nitrogen	$62^{\circ}5, 20^{\circ}5$	41.5	623.5	$14^{\circ}84$
7.	Boiling hydrogen and melting hydrogen	$20^{\circ}5, ?$	?	51.0	?
8.	Boiling hydrogen—solid hydrogen about 20 m.m..	$20^{\circ}5, ?$	?	64.0	?

dE/dt is the quotient of the mean galvanometer reading by the difference of the temperatures in the third column.

On plotting the first six of these results, the first, second, and sixth and means of the other three—viz., $dE/dt = 21\cdot59$ at $t = 87^{\circ}$ —lie nearly on a continuous curve (Fig. 1). The continuity of the curve, without any approach to abrupt change of form, even in the region of liquid hydrogen, shows that a silver soldered German-silver platinum couple is an efficient instrument for the determination of the lowest temperatures hitherto reached. For example, we may employ the curve (Fig. 1) to determine the temperature of the hydrogen under exhaustion in observation No. 8. A graphical examination of the curve in the neighbourhood of the boiling-point of hydrogen shows that we may write—

$$dE/dt = 10\cdot2 + \frac{1}{2}(t - 18), \text{ or } dE/dt = 7\cdot2 + \frac{1}{4}t,$$

as an equation holding true for a few degrees above or below 18° absolute. Hence, if x be the required temperature, we have—

$$\frac{64}{20\cdot5 + x} = 7\cdot2 + \frac{20\cdot5 + x}{12} \text{ or } 20x^2 + 1728x = 28469,$$

one of whose roots is $14\cdot15$. From the graphical analysis

* A Paper read before the Royal Society, June 8, 1905.

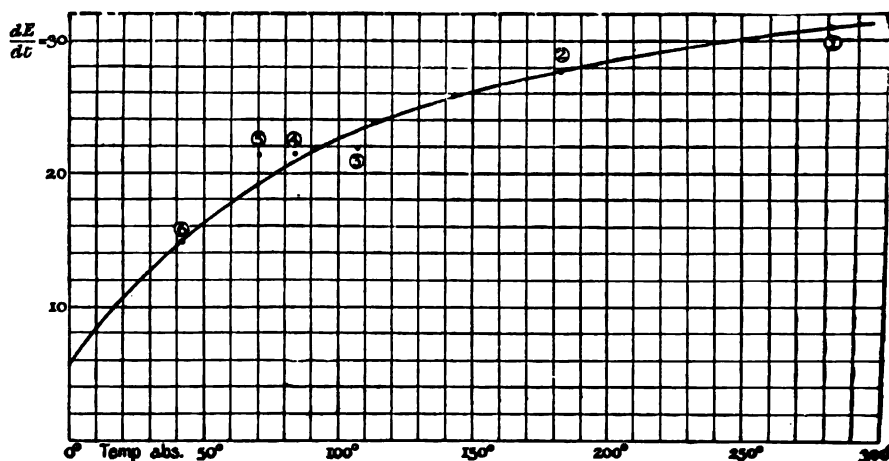


FIG. 1.—THERMO-ELECTRIC JUNCTION.

of the curve, therefore, we find the temperature of the hydrogen under exhaustion in the last observation to be 14.15° absolute, or some 6.3° below the boiling-point. Similarly, for observation No. 7 the temperature is found to be 15.50° .

From the results a curve with electromotive force, E , as ordinate, to absolute temperature, t , as abscissa, may be drawn, and this may be taken as a parabola, with the equation—

$$(t+a)^2 = p(E+b) \quad (1).$$

For another point, t' , E' , we have—

$$(t'+a)^2 = p(E'+b),$$

whence, subtracting,—

$$E' - E = p^{-1} (t' - t) (t' + t + 2a) \quad (2).$$

Any pair of observations will give p and a , after which, assuming any given point, for example H_{BP} , as origin, and putting $t = 20.5^\circ$ absolute and T for $t' - 20.5$, we get the equation connecting difference of electromotive force and difference of temperature—

$$E' - E = p^{-1} T \{T + 2(t+a)\}.$$

An average value of dE/dt from (2) is equal to $\frac{E' - E}{t' - t}$,

that is $= p^{-1} (t' + t + 2a)$; but the correct value of dE/dt at a given point is, from (1),—

$$\frac{dE}{dt} = \frac{2}{p} (t+a).$$

Now the fact that the Tait line does not remain straight, but bends downwards as we approach the absolute zero, indicates that the parabola is being distorted as we approach its vertex, just as if the vertex were being pushed up. To look for a straight line near the vertex therefore we must keep to observations near the vertex. I have therefore taken the four sets, Nos. 3, 4, 5, 6, from the table, similarly marked on the diagram (Fig. 2), in which the highest extends from ethylene exhausted, 123.5° absolute, to the boiling-point of oxygen, 90.5° absolute.

These corrected observations are given in Table II.

TABLE II.

Range.	Temp. abs.	$E' - E$.	$t' - t$.	$t' + t$.
(3). Ethylene exh. to boiling oxygen..	123.5—90.5	724.0	33	214
(4). Boiling oxygen to boiling nitrogen.	90.5—77.5	279.0	13	168
(5). Boiling nitrogen to melting nitrogen	77.5—62.5	320.7	15	140
(6). Melting nitrogen to boiling hydrogen	62.5—20.5	623.5	42	83

Hence equations of form (2), re-arranged more conveniently for calculation are—

$$(3). \quad 33 \times 214 + 2a.33 = 724 \quad \text{or} \quad 214 + 2a = 21.9^\circ.$$

$$(4). \quad 13 \times 168 + 2a.13 = 279 \quad \text{"} \quad 168 + 2a = 21.5^\circ.$$

$$(5). \quad 15 \times 140 + 2a.15 = 320.7 \quad \text{"} \quad 140 + 2a = 21.4^\circ.$$

$$(6). \quad 42 \times 83 + 2a.42 = 623.5 \quad \text{"} \quad 83 + 2a = 14.8^\circ.$$

Taking (3) and (6), we get $p = 18.45$ and $2a = 190.0$.

Therefore $E = \frac{1}{18.45} T (T + 231)$, reckoning from H_{BP} as origin. Hence for $E = -51$ we have—

$$(T + 115.5)^2 = 115.5^2 - 51 \times 18.45 = 111.4^2.$$

Therefore $T = -4.1$, or H_{BP} is 4.1° below H_{BP} , or is 16.4° absolute.

For $E = -64$, $T = -5.23$, or $H_{exh.}$ is 5.23° below H_{BP} , or is 15.27° absolute.

From (3) and (6), reckoning from H_{BP} as origin, we get—

$$dE/dt = 12.52 + 0.108T.$$

There is hardly a doubt that dE/dt at H_{BP} is not so great as 12.52 , so that, as was anticipated, the $H_{exh.}$ — O_{BP} observations are too far away from H_{BP} to give a workable formula.

Taking (4) and (6) we get $p = 12.69$ and $2a = 104.8$.

Therefore $E = \frac{1}{12.69} T (T + 145.8)$, reckoning from H_{BP} as origin. Hence for $E = -51$ we have—

$$(T + 72.9)^2 = 72.9^2 - 51 \times 12.69 = 68.3^2.$$

Therefore $T = -4.6$, or H_{BP} is 4.6° below H_{BP} , or is 15.9° absolute.

For $E = -64$, $T = -5.8$, or $H_{exh.}$ is 5.8° below H_{BP} , or is 14.7° absolute.

From (4) and (6), reckoning from H_{BP} as origin, we get—

$$dE/dt = 11.49 + 0.158T.$$

In like manner from (5) and (6) we get $p = 8.64$ and

$2a = 44.8$, whence $E = \frac{1}{8.64} T (T + 85.8)$, reckoning from H_{BP} as origin.

For $E = -51$ we get $(T + 42.9)^2 = 42.9^2 - 51 \times 8.64 = 37.4^2$, and therefore $T = -5.5$, giving the melting-point of hydrogen 5.5° below its boiling-point, or 15.0° absolute; and when $E = -64$, $T = -7.0$, or the temperature of the hydrogen under exhaustion was 13.5° absolute. Observations (5) and (6) also lead to the equation—

$$dE/dt = 9.931 + 0.231T,$$

with the boiling-point of hydrogen as origin of temperature.

It is of importance to examine how an alteration of any

of the constants in the formulæ employed affects the temperature deduced.

Choosing any assigned temperature as origin, the value of dE/dt at T^0 from that origin is given by an equation of the form $dE/dt = m + nT$.

But if the value assigned to dE/dt is obtained by dividing the difference of electromotive force D through the range of temperature T by T , then this value of dE/dt must be assigned to the mean temperature $\frac{1}{2}T$, and the formula becomes—

$$D/T = m + \frac{1}{2}nT, \text{ or } D = mT + \frac{1}{2}nT^2,$$

a quadratic for the determination of T when D is known.

When the constant n alone varies, differentiating we have—

$$dT = -\frac{1}{2} \frac{T^2}{m + \frac{1}{2}nT} dn.$$

Thus if $m = 9.931$, $n = 0.231$, and $T = -7^\circ$, we get—

$$dT = -\frac{49}{16.628} dn = -2.947 dn;$$

hence for $dn = -0.031$, $dT = +0.101$, showing that an

alteration of n from 0.231 to 0.200 would only alter T from -7.0° to -6.9° ; or, roughly, a 10 per cent change in n at this temperature would only affect the temperature by 1 per cent.

When the constant m alone varies, differentiating we have—

$$dT = -\frac{T}{m + \frac{1}{2}nT} dm;$$

hence, in the same circumstances as before,—

$$dT = -\frac{-7}{8.314} dm = 0.842 dm;$$

and thus, for a change $dm = 0.119$, the corresponding change of temperature is $dT = 0.100$, or if m were altered from 9.931 to 10.050, T would again be changed only from -7.0° to -6.9° .

We may in a similar manner consider the effect of an error in the reading D on the deduced temperature.

$$\text{For } dD = (m + \frac{1}{2}nT)dT, \text{ or } dT = \frac{1}{m + \frac{1}{2}nT} dD,$$

giving, in the case already considered, $dT = 0.12 dD$, so that an error of a unit on D would only alter the value of T by an eighth of a degree.

These numerical results may be summarised by saying that, in the neighbourhood of the temperature of solid hydrogen under exhaustion, it would require an alteration of 1½ per cent in the values of D or m , and as much as 13 per cent in the value of n , to alter the value of T by one-tenth of a degree.

In general it may be noted that, for an alteration of the same actual (but small) magnitude in the values of n , m , and D respectively, the corresponding alterations of T are proportional to $\frac{1}{2}T^2$, T , and 1.

The general results with the German-silver platinum junction are summarised in Table III., the typical equation being $dE/dt = m + nT$.

TABLE III.

Source of constants.	m .	n .	Melting-point of hydrogen.	Solid hydrogen exhausted.
(3) and (6).	12.52	0.108	16.4°	15.27°
(4) " (6).	11.49	0.158	15.9	14.7
(5) " (6).	9.931	0.231	15.0	13.5
Graphically	10.2	0.167	15.5	14.15
Mean..	—	—	15.7	14.4

For reasons already mentioned, the temperatures deduced from the (5) and (6) set of experiments are in all probability the most accurate in the thermo-electric series of observations.

It is interesting to compare these results with those given in my former paper on the "Boiling-point of Liquid Hydrogen Determined by Hydrogen and Helium Gas Thermometers" (*Proc. Roy. Soc.*, 1901, vol. lxxiii.). Although the main object of that paper was the accurate determination of the boiling-point of hydrogen, I included in the experiments the recorded temperature of solid hydrogen under exhaustion of from 30 to 40 m.m., as given by a hydrogen gas thermometer filled initially at a pressure of 269.8 m.m. at 0°C . This thermometer gave the boiling-point of hydrogen as 19.63° , and the solid under exhaustion as 14.34° ; in other words, the gas thermometer value is just about a mean of the results given by the thermo-junction. This is, so far, confirmatory of the reliability of the thermo-junction as a thermometric agent at the lowest steady temperature we can command.

Although it is not recorded in the paper on the "Boiling-point of Hydrogen," I found that the same helium thermometer which I used for determining the boiling-point gave in exhausted solid hydrogen the temperature of 13.65° , but as the helium had to be corrected for the presence of a small amount of neon, the result might be a little too low. My intention at the time was to defer the consideration of the temperature of solid hydrogen for a further communication to the Royal Society, as distinctly stated in the original paper.

It is true that in a paper on "Solid Hydrogen," read at the British Association in 1899 (*Nature*, September 21, 1899), that is two years before, I gave the approximate melting-point of hydrogen as between 16° and 17° absolute. This value was based on observing the melting-point pressure of solid hydrogen as being about 55 m.m., and therefrom calculating what the temperature should be at this pressure by means of a mean Rankine formula. From the later experiments contained in my paper of 1901 a more accurate Rankine formula can be deduced, viz.,—

$$\log p_H = 6.2874 - 68.02/t,$$

and this gives the approximate temperature of 14.96° as corresponding to 55 m.m., thus bringing the melting-point given by the gas thermometer into substantial agreement with the lowest thermoelectric value.

As a record of the behaviour of the German-silver platinum thermo-junction Table IV. has been calculated from the equations derived from the set of observations (5) and (6), namely:—

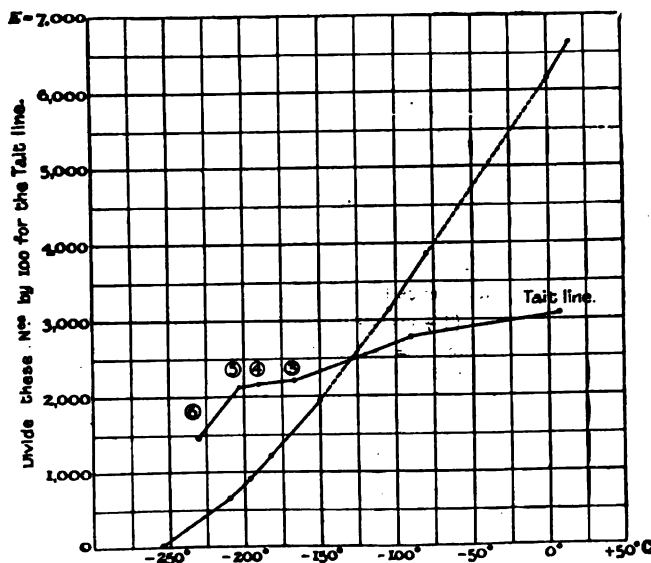


FIG. 2.—THERMO-ELECTRIC JUNCTION.

$$E = \frac{1}{8.64} T (T + 85.8) \text{ and } \frac{dE}{dt} = 9.931 + 0.231 T,$$

when one of the junctions of the couple is assumed to be kept in boiling hydrogen, and the other either falls or rises through a range of some 15° on either side of this temperature, which is about 20.5° absolute. These values show that, at as low a temperature as 6° absolute, the sensibility of this couple is still half what it was at 20.5° absolute, and therefore that, unless some absolute breakdown in the law connecting electromotive force and temperature below 14° takes place, it must continue to be an excellent thermometer, and will record temperature with considerable accuracy down to the boiling-point of helium, which is about 5° or 6° absolute. A further paper will detail the results obtained in the study of the behaviour of helium at low temperatures.

TABLE IV.

t abs.	dE/dt .	E .
35°	13.281	168.32
32	12.588	129.51
29	11.895	92.77
26	11.202	58.09
23	10.509	25.55
20.5	9.931	nil
18	9.354	- 24.10
15	8.661	- 51.12
12	7.968	- 76.05
9	7.275	- 98.90
6	6.582	- 119.70

I am indebted to Mr. T. D. H. Dickson, M.A., of St. Peter's College, Cambridge, for help in the discussion of the results, and to Mr. Robert Lennox, F.C.S., for assistance in the conduct of the experiments.

THE WEIGHTS OF OXYGEN, NITROGEN, AND HYDROGEN.

By C. J. T. HANSSSEN, C.E.

PROFESSOR SIR JAMES DEWAR's excellent experiments on oxygen, nitrogen, and hydrogen, described in a paper read before the Royal Society, March 17, 1904, and published in the *CHEMICAL NEWS* (vol. lxxxix., pp. 205, 217), are of high importance, as in these experiments the liquefied and solidified gases operated upon have, in the process of cooling, been more perfectly purified than is possible by chemical means; and, being contracted to a comparatively very small volume, may be weighed more exactly than by the usual weighing of gas in large glass balloons.

Sir James Dewar might at the same time have settled the important and vexed question of the absolute and the atomic weight of these gases; this, however, has not been his intention. He has taken the weight of 1 litre of gas at 0° C. and 760 m.m. pressure as—

Oxygen		= 1.43 grms.
Nitrogen		= 1.2564 "
Hydrogen		= 0.0899 "

The volume of the condensing flask was—

For O at $+15^{\circ}$ C.		= 23.9212 c.c.
„ N and H at $+14.2^{\circ}$ C.		= 22.1454 "

The coefficient of cubical expansion by heat (or contraction by cold) of glass was taken = $0.000250 = 1/40000$ of volume for 1° C. from $+15^{\circ}$ C. down to the lowest temperatures.

If the volumes of gas used in the experiments are reduced to uniform temperature, $\pm 0^{\circ}$ C. = 273° C. abs., and to 760 m.m. pressure, we get—

Table I.	1. Oxygen	..	18610596 cubic m.m.
„	2. „	..	19468555 „
„	4. „	..	23686880 „
Table II.	1. Nitrogen	..	14100550 „
„	3. „	..	17969380 „
Table III.	1. Hydrogen	..	17134642 „
„	3. „	..	18670470 „

The volume of the condensing flask for O, which at $+15^{\circ}$ C. (= 288° C. abs.) is = 239212 c.c., will, according to the coefficient of contraction adopted in the experiments, be—

Table I.	1. At -182.5° C. (= 90.5° C. abs.)	= 23803.089	Cubic m.m.
„	2. „ -195.5° C. (= 77.5° C. abs.)	= 23795.116	
„	4. „ -252.5° C. (= 20.5° C. abs.)	= 23761.227	

The condensing flask for N and H, which at $+14.2^{\circ}$ C. (= 287.2° C. abs.) is = 22.1454 c.c., is—

Table II.	1. At 195.5° C. (= 77.5° C. abs.)	= 22029.303	Cubic m.m.
„ III.	1. „ 252.5° C. (= 20.5° C. abs.)	= 21997.746	
„ III.	3. „ 259.9° C. (= 13.1° C. abs.)	= 21993.649	

The volume of gas at 273° C. abs. and 760 m.m. pressure, condensed and filling the flask, = $\frac{\text{Volume of gas}}{\text{Volume of flask}} =$ 1 volume condensed gas.

TABLE I.—Oxygen.

$^{\circ}$ C. abs.	Cubic m.m.	Vols. gas.
1. 90.5	$\frac{18610596}{23803.089}$	= 781.856 = 1 vol. liquid O 90.5°
2. 77.5	$\frac{19468555}{23795.116}$	= 818.174 = 1 vol. liquid O 77.5°
4. 20.5	$\frac{23686880}{23761.227}$	= 996.871 = 1 vol. solid O 20.5°

TABLE II.—Nitrogen.

$^{\circ}$ C. abs.	Cubic m.m.	Vols. gas.
1. 77.5	$\frac{14100550}{22029.303}$	= 640.077 = 1 vol. liquid N 77.5°
3. 20.5	$\frac{17969380}{21997.746}$	= 816.874 = 1 vol. solid N 20.5°

TABLE III.—Hydrogen.

$^{\circ}$ C. abs.	Cubic m.m.	Vols. gas.
1. 20.5	$\frac{17134642}{21997.746}$	= 778.927 = 1 vol. liquid H = 20.5°
3. 13.1	$\frac{18670470}{21993.649}$	= 848.903 = 1 vol. solid H = 13.1°

We may conveniently take these volumes = litres. Then, 781.856 litres O gas of 273° C. abs. and 760 m.m. pressure are = 1 litre liquid O of 90.5° C. abs., and multiplying by the adopted weight per litre of gas, we get the specific gravity of the condensed liquid or solid gas:—

TABLE I.—Oxygen (273° C. abs.).

C. abs.	Litres.	Grms.	Grms.	C. abs.
90.5°	781.856×1.43	= 1118.05408	= 1 litre liquid O	90.5°
77.5°	818.174×1.43	= 1169.98882	= 1 litre liquid O	77.5°
20.5°	996.871×1.43	= 1425.52553	= 1 litre solid O	20.5°

TABLE II.—Nitrogen.

C. abs.	Litres.	Grms.	Grms.	C. abs.
77.5°	640.077×1.2564	= 804.19274	= 1 litre liquid N	77.5°
20.5°	816.874×1.2564	= 1026.32049	= 1 litre solid N	20.5°

TABLE III.—Hydrogen.

C. abs.	Litres.	Grms.	Grms.	C. abs.
20.5°	778.927×0.0899	= 70.02554	= 1 litre liquid H	20.5°
13.1°	848.903×0.0899	= 76.30538	= 1 litre solid H	13.1°

These values agree very closely with the densities in Professor Dewar's Tables I., II., and III. (column d).

But these densities are correct only if the adopted coefficient of expansion of glass and the weight per litre of O, N, and H gas of 273° C. abs. and 760 m.m. pressure (London latitude) are correct.

That the coefficient of expansion of glass = 1/40000 of the volume down to the lowest temperatures appears to be questionable, although Prof. Dewar has adopted it.

All kinds of glass, fused silica not excepted, expand at +300° C. three to four times more than at +100° C., and at 0° absolute the expansion evidently must be = 0.

The proper scale for cubical expansion of glass by heat (and contraction by cold) to suit the prevailing circumstances must be a curve, which, very nearly correct, may be found thus:—

Suppose the condensing flask at +0° C. (273° C. abs.) contains 1000000 volume-units, it will then expand by heat or contract by cold at the rate $\frac{n^{\circ} \text{C. abs.}}{10}$. At absolute 0° (= -273° C.) it will be decreased.

$\frac{273^{\circ}}{10} = \frac{74529}{10} = 7453$ vol.-units and remain 1000000 - 7453 = 992547 volume-units; at $\pm 0^{\circ} \text{C.} (= 273^{\circ} \text{C. abs.})$ it is 1000000 volume-units, and—

°C.	°C. abs.		Vol.-units.
At +15 (= 288)	$\frac{288^{\circ}}{10}$	= 8294 + 992547 =	1000841
" +14.7 (= 287.2)	$\frac{287.2^{\circ}}{10}$	= 8248 + 992547 =	1000795
"	$\frac{90.5^{\circ}}{10}$	= 819 + 992547 =	993366
"	$\frac{77.5^{\circ}}{10}$	= 601 + 992547 =	993148
"	$\frac{20.5^{\circ}}{10}$	= 43 + 992547 =	992589
"	$\frac{13.1^{\circ}}{10}$	= 17 + 992547 =	992564
" +300 (= 573)	$\frac{573^{\circ}}{10}$	= 32833 + 992547 =	1025380

Professor Dewar's condensing flask for oxygen, which at +15° C. (288° C. absolute) has volume 23921 cubic m.m., will, at this rate of contraction,—

At 90.5° C. abs. contain 23742.540 cubic m.m.
" 77.5° " " 23737.330 "
" 20.5° " " 23733.529 "

And the flask for nitrogen and hydrogen, which at +14.2° C. (287.2° C. abs.) contains 22145.4 cubic m.m., will—

At 77.5° C. abs. contain 21976.180 cubic m.m.
" 20.5° " " 21972.662 "
" 13.1° " " 21963.258 "

The weight given for nitrogen gas at 273° C. abs. and 760 m.m. pressure seems too high. 1.2564 grms. per litre, if O is 1.43 would be = 14.05751 atomic weight of N if O is 16; while the International Table of Atomic Weights (1904) only has 14.04 for N, and in R. W. Gray's and other experiments it varies between 13.990, 14.004, and 14.007. (See CHEMICAL NEWS, xc., p. 269; xci., pp. 44, 240, 292).

The volume of gas at 273° C. abs. and 760 m.m. pressure condensed and filling the flask = $\frac{\text{Volume of gas}}{\text{Volume of flask}}$ forming 1 volume liquid or solid gas.

TABLE I.—Oxygen.

°C. abs.	Cubic m.m.	Volumes gas.
1. 90.5	$\frac{18610596}{23742.540}$	= 783.850 form 1 volume liquid.
2. 77.5	$\frac{19468555}{23737.330}$	= 820.024 " " liquid.
4. 20.5	$\frac{23686880}{23733.529}$	= 998.035 " " solid.

TABLE II.—Nitrogen.

°C. abs.	Cubic m.m.	Volumes gas.
1. 77.5	$\frac{14100550}{21976.180}$	= 641.629 form 1 volume liquid.
3. 20.5	$\frac{17969380}{21972.662}$	= 817.807 " " solid.

TABLE III.—Hydrogen.

°C. abs.	Cubic m.m.	Volumes gas.
1. 20.5	$\frac{17134642}{21972.662}$	= 779.816 form 1 volume liquid.
3. 13.1	$\frac{18670470}{21963.697}$	= 850.077 " " solid.

We may, as above, take these volumes = litres, and find the density or the weight per litre of liquid and solid O, N, and H by multiplying by the weight per litre of gas of 273° C. abs. and 760 m.m. pressure. If we multiply by Professor Dewar's weights we get—

Oxygen.

°C. abs.	litres.	Grms.	Grms.
90.5	783.850	$\times 1.43$	= 1120.90550 = 1 litre liquid O.
77.5	820.024	$\times 1.43$	= 1172.63432 = 1 " liquid O.
20.5	998.035	$\times 1.43$	= 1427.19005 = 1 " solid O.

Nitrogen.

77.5	641.629	$\times 1.2564$	= 806.14268 = 1 " liquid N.
20.5	817.807	$\times 1.2564$	= 1027.49271 = 1 " solid N.

Hydrogen.

20.5	779.816	$\times 0.0899$	= 70.10546 = 1 " liquid H.
13.1	850.077	$\times 0.0899$	= 76.21922 = 1 " solid H.

But these weights per litre (O = 16) correspond to the atomic weights N = 14.575, C = 12.007, H = 1.0076, &c.—all determined before argon, helium, neon, and other gases which are contained in our atmosphere, in water, and in minerals, were known or suspected to exist, and before gases could be separated and purified by distillation at very low temperatures. With the means now available, chemists and physicists will soon ascertain and remove the last traces of known or still unknown gases which combined with H make it appear heavier than one-sixteenth of O. The atomic weight of C., which a few years ago was taken = 12.007, is now acknowledged to be 12.000 (O = 16.00), and so will N soon be = 14 and H = 1.

In the hope that the number of elements whose atomic weights now are expressed by integers may very soon be considerably increased, I multiply the volumes of gases found by the weights per litre,—

Atomic weight.	London latitude.	Latitude 41° 10'.
O = 16	1.42992 grms.	10/7 grms.
N = 14	1.25118 "	10/8 "
H = 1	0.08937 "	5/56 "

and find the specific gravity and the weight per litre of the condensed gases (London latitude):—

273° C. abs.	760 m.m.	
°C. abs.	Litres.	Grms.
O. 90.5	783.850	$\times 1.42992$ = 1120.84279 = 1 litre liquid.
77.5	820.024	$\times 1.42992$ = 1172.56872 = 1 " "
20.5	998.035	$\times 1.42992$ = 1427.11021 = 1 " solid.
N. 77.5	641.629	$\times 1.25118$ = 802.79337 = 1 " liquid.
20.5	817.807	$\times 1.25118$ = 1023.22376 = 1 " solid.
H. 20.5	779.816	$\times 0.08937$ = 69.69216 = 1 " liquid.
13.1	850.077	$\times 0.08937$ = 75.97138 = 1 " solid.

Copenhagen V., Valdemarsgade 3.

THE
DEVELOPMENT OF SPECTRO-CHEMISTRY.*

By Professor JULIUS WILHELM BRÜHL, Ph.D., Sc.D.,
Hon. Mem. R.I., Professor in the University of Heidelberg.

ASSOCIATED as I am with Great Britain in my capacity as a Member of the Royal Institution, it is a special pleasure to me this evening to sketch to you the development of a branch of scientific study, the early history of which was enacted in this country—a country to which for many years I have been bound by close ties of sympathy. Many of you know already, and the others will see this evening, that I am in especial measure indebted to the science of this country for stimulus and encouragement in my own studies. It is a source of deep satisfaction to me to testify here to the gratitude which I owe to British science.

I.

1. Last August it was my privilege to attend the Meeting of the British Association on the classic ground of Cambridge, and one sunny afternoon I found my way into that peculiarly effective example of collegiate architecture, the Chapel of Trinity College. The organ was playing Bach's Passacaglia, and I sat down quietly at the foot of the marble statue which bears the inscription:—

NEWTON.

Qui genus humanum ingenio superavit.

The empty chapel was filled with harmony and with memories of the great man who once had sojourned there. And my thoughts wandered back to the past.

In 1666, almost two and a-half centuries ago, Isaac Newton, then a young bachelor, had decomposed a beam of sunshine, discovered the diverse refrangibility of the coloured rays, and explained the phenomena of dispersion.

The founder of scientific optics was also the first to perceive a connection between differences in the composition of various natural bodies and their power of transmitting light.

Newton observed that oils, amber, sulphur, and other combustible bodies possess great refractive power, and he made the remarkable statement that the diamond must also be combustible, because it refracts light so powerfully. This statement is indeed remarkable when we remember that in those distant times no one had any idea of the chemical composition of the diamond, or any conception of the nature of combustion.

But centuries of patient work were needed in order to recognise clearly the connection between the chemical composition of different bodies and their power of refracting and dispersing light in different ways, *i.e.*, of producing differently constituted spectra. To account for this connection has become the task of "Spectro-chemistry."

2. Newton was also the first to fix a standard for measuring the refractive power of bodies. Starting from the emanation theory of light which he had himself founded, he diminished the square of the refractive index, n , by unity and regarded—

$$n^2 - 1$$

as the expression for the refractive power. This power, reduced to constant density, *i.e.*, divided by the specific gravity d of the body:—

$$\frac{n^2 - 1}{d}$$

was called by Newton the "absolute refractive power."

3. It was fully a hundred years later that Laplace, in his celebrated "*Mécanique céleste*," laid down the principle that the expression for refraction, derived from Newton's emanation theory, must for one and the same substance be unaffected by changes in density caused by temperature and pressure—unaffected, that is, by the accidental density of a substance.

4. The hitherto purely hypothetical formula for refraction acquired further scientific importance from the researches of Biot and Arago (1806), and Dulong (1826), on the refractive powers of gases and vapours. These, the first quantitative measurements of refractivity, seemed actually to confirm the theory that Newton's formula denotes a constant quantity which always remains unaffected by the accidents of temperature and pressure.

But with the triumph of the modern wave-theory of light, Newton's expression for refraction, $\frac{n^2 - 1}{d}$, lost its theoretical importance. New experiments soon showed that even its supposed independence of temperature and pressure did not in fact exist.

II.

5. In 1858, John Hall Gladstone, who was for some time Professor in this Institution, began his splendid series of optical researches, which he pursued with great success for over forty years. At first in collaboration with the Rev. T. Pelham Dale he investigated the dependence of refractivity on temperature in the case of fluid substances. The important fact was at once established that Newton's expression for refraction $\frac{n^2 - 1}{d}$, is not constant, but varies considerably with the temperature. On the other hand, it was found that the more simple ratio—

$$\frac{n - 1}{d}$$

remains practically constant.

Now this ratio, just like the Newtonian constant confirmed by Biot and Arago, and by Dulong, applies also to gases and vapours. As, in the case of gases, the refractive index is very little different from unity, the numerical value of $\frac{n^2 - 1}{d}$ is almost exactly twice that of $\frac{n - 1}{d}$.

III.

6. Soon after 1860, Hans Landolt came forward with his optical researches. He began by confirming the results of Gladstone and Dale. He proceeded a step further, however, by following the example of Berthelot, and comparing the refractivity not of equal, but of molecular quantities of the substances. If P represents the molecular weight, the product $\left(\frac{n - 1}{d}\right)P$ is the molecular refraction.

7. Landolt examined particularly the fundamental question whether a different grouping of the same number of atoms of the same elements—which is the cause of isomerism—has any influence on the optical properties of bodies.

He established the important fact that only the relative weight of the elements is of influence on the molecular refraction of a compound, while the different grouping of the atoms has no appreciable effect; and this made it possible to determine the atomic refractions of the elements. The atomic refraction of carbon, for instance, was obtained by comparing the molecular refractions of two compounds which differed only by one atom of carbon; and in a similar manner the atomic refractions of the remaining elements were determined.

With the aid of these constants it was now possible to calculate *a priori* the molecular refraction of many organic compounds from the elements composing them, and Landolt showed that the calculated molecular refractions agreed very well with those determined by experiment.

8. Gladstone, in the course of his researches, was able to confirm Landolt's results in many cases. But he also found a considerable number of substances in which the observed molecular refraction was completely at variance with that obtained by adding the atomic refractions together. The exceptions were so numerous, that they really seemed to overthrow the whole law of summation.

IV.

9. Shortly before 1880, when I was studying the literature of chemical optics, a brief note published by Gladstone in

* A Lecture delivered at the Royal Institution, May 26, 1905.

the *Journal of the Chemical Society* for May, 1870, excited my attention and curiosity. The author there discusses the exceptions to Landolt's rule of summation. He shows firstly that in all such cases the molecular refraction is never found to be too small, but always too great. Then he shows that whole classes of compounds behave in this abnormal fashion.

10. All optically abnormal compounds proved to be rich in carbon. Gladstone therefore examined the effect which a gradual increase of carbon in the composition of a body exerted on its refractivity. He found that there actually was an increase in the excess of the experimental as compared with the calculated molecular refraction, but the increase was not regular enough to explain the anomalies.

The saturated hydrocarbons or *paraffins*, of the general composition C_nH_{2n+2} , showed *normal* molecular refraction.

Also the *olefines*, containing two atoms less of hydrogen, were found normal by Gladstone.

On the other hand, the hydrocarbons containing six atoms less of hydrogen, viz., the *terpenes*, gave molecular refractions about 3 units larger than would correspond to their composition.

With the aromatic hydrocarbons, such as benzene, toluene, &c., containing eight atoms less of hydrogen, this abnormal excess amounted to 6 units:—

Paraffins	(C_nH_{2n+2})	Normal
Olefines	" $-H_2$	"
Terpenes	" $-H_6$	" +3
Benzene and derivatives ..	" $-H_8$	" +6

With still further decrease in the quantity of hydrogen contained (*i.e.*, with further increase of carbon), there resulted greater and greater refractive increments.

The last member of the series, however—pure carbon without any hydrogen, represented by the diamond—proved to be perfectly normal in its optical properties.

V.

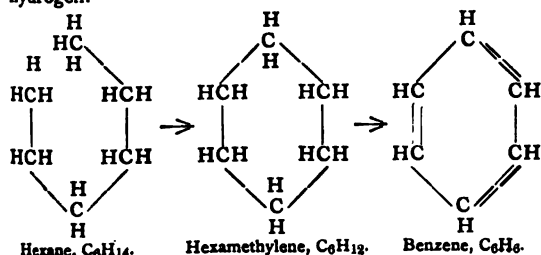
11. François Arago, when sketching in his celebrated "Eloges" the life and work of Thomas Young, relates that the latter was led to his fundamental discovery of the interference of light by nothing more extraordinary than soap-bubbles. In this connection Arago remarks that it is one of the most precious gifts to be able to wonder at the right time.

Gladstone's observations just mentioned had been known almost ten years without anybody's surprise being excited. When his short note came into my hands, I was fortunate enough to begin wondering at the right time.

It seemed to me really extraordinarily remarkable that all optically abnormal substances, without exception, gave a too *high* molecular refraction. It was no less astonishing to me that the saturated hydrocarbons were optically normal, but became more and more abnormal at successive withdrawals of hydrogen—while pure carbon, uncombined with hydrogen, is again completely normal.

But I was most particularly struck by the quantitative amount of the abnormality in the case of benzene compounds, especially their refractive increment of *six* units. The number 6 fascinated me. I could not help thinking that therein lay the key to the mystery, and I lost no time in making use of it.

12. According to Kekulé's ingenious hypothesis we can imagine benzene, C_6H_6 , to have arisen from the saturated hydrocarbon hexane, C_6H_{14} , by successive removal of hydrogen.



Thus altogether four pairs of hydrogen atoms have been removed. The elimination of the first pair was made the occasion to form another *simple* carbon bond like those already present in hexane, and with it the ring was closed. The splitting-off of the other three pairs of hydrogen atoms, on the other hand, resulted in the formation of three *double* bonds of carbon atoms—a kind of bond which does not occur in the optically normal hexane.

Now Gladstone had found that benzene exhibits a refractive increment of 6 units. Reading this I was struck in a moment by the thought:—Might not this abnormal refractive increment of benzene be due to its double carbon bonds, which are absent in the optically normal hexane?

And if this were so, I went on to reason, since *three* double bonds in benzene correspond to a refractive increment of 6 units, therefore *one* double bond must entail the increment of 2.

These ideas received no support whatever from the then known facts. For Gladstone had stated expressly that the olefines, *i.e.*, open-chain hydrocarbons, containing *one* double carbon bond, were optically *normal*.

However, I did not allow myself to be discouraged; and, behold! my expectations were confirmed by the very first experiment. The olefine examined not only proved to be optically abnormal, but gave the predicted refractive increment of 2 units, corresponding to the presence of *one* double carbon bond.

Gladstone, therefore, as I had supposed, was mistaken in this case. Further experiments proved that not one of the olefines was optically normal. Without exception they gave the refractive increment of 2 units, one-third of that of benzene.

I next proceeded to examine the diolefines—substances which contain *two* double carbon bonds. Here also, in conformity with expectation, a constant refractive increment was found, double as large as that of the olefines and two-thirds of that of benzene:—

Paraffins	(C_nH_{2n+2})	Normal
Olefines	" $-H_2$	" +2
Diolefines	" $-H_4$	" +4
Benzene compounds ..	" $-H_8$	" +6

The dimensions of our subject this evening prevent the detailed demonstration of these important facts by experiment. I will only show you that the spectrum of a saturated hydrocarbon (a paraffin) is distinguishable at a glance from that of a substance containing double bonds.

On this screen we project the electric spectrum of metallic calcium. First we cause the rays of light to pass through a prism filled with paraffin-oil. Then we exchange this prism for another, filled with a substance containing atoms linked by double bonds. (Experiment).

In the second case you observe, firstly, a much greater deviation of the whole spectrum, *i.e.*, greater *refraction*, and, secondly, far wider intervals between the coloured lines of the spectrum, *i.e.*, greater *dispersion*, which is usually correlative to the refraction.

13. Thus quantitative experimental confirmation was obtained for the view that abnormal refractive increments which increase with the diminution of hydrogen contained in the substances, are caused by the presence of double carbon bonds.

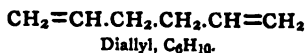
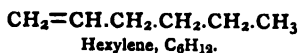
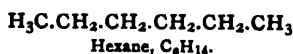
At the same time, however, the experiments yielded a second result of fundamental importance. The olefines contain 2, and the diolefines 4 atoms of hydrogen less than the paraffins. Similarly the refractive increment of the olefines is 2, and of the diolefines 4.

Benzene, C_6H_6 , contains 8 atoms of hydrogen less than the corresponding paraffin, hexane, C_6H_{14} . The increment of benzene, however, amounts not to 8, but to 6! Thus in the formation of benzene from hexane, 2 atoms of hydrogen have been eliminated without influence on the refractive increment of the product.

But in the formation of benzene from hexane, 2 atoms of hydrogen have been employed to close the ring (see diagram, at Section 12). The withdrawal of these two atoms and

the closing of the ring have therefore taken place without causing any optical anomaly.

In the formation of the olefines and diolefines from the paraffins, however, there is no closing of the ring. These substances are of open-chain structure, and every removal of 2 hydrogen atoms corresponds here to the creation of a double carbon bond:—



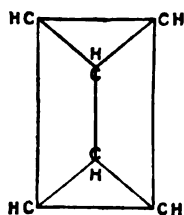
Hence, also, the refractive increment of the olefines and diolefines is directly proportional to the number of hydrogen atoms removed from the paraffin.

From all this it follows that the removal of hydrogen atoms causes optical anomalies only where double carbon bonds are created by the process. *The splitting-off of hydrogen which results in the closing of a ring is, on the other hand, without abnormal optical influence, and produces no refractive increment.*

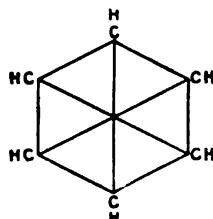
This latter principle, which has since been confirmed many times by experiment, has proved of the same importance as the first in the investigation of the chemical structure of bodies.

14. A few examples will show how these two principles can be utilised for the discovery of chemical structure.

Besides the formula already mentioned for benzene—that suggested by Kekulé—several others have been proposed, e.g., those by Ladenburg and Claus:—



Ladenburg.



Claus.

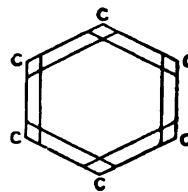
Neither of these graphic formulæ is reconcilable with the results of spectro-chemical investigation, because the neighbouring carbon atoms contained in them are associated only by single cycloid or ring-closing affinities, and not by any so-called double bonds. Substances of this kind should be optically normal, while benzene and its derivatives are, as a matter of fact abnormal. Kekulé's formula for benzene is really the only graphic representation of its structure in a single plane which is confirmed by chemical optics.

Thus it can be at once determined by optical methods whether a given body belongs to the paraffinoid, olefinoid, or cycloid products; whether these products contain double bonds or not; and if so, how many.

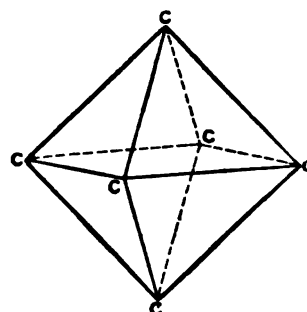
Now, too, we can imagine why the diamond, i.e., pure crystallised carbon, is, as already mentioned, optically normal. We obtain an idea of the mineral's chemical constitution, and of the way in which the atoms of carbon are perhaps combined in the sparkling gem.

For the reasons already stated, the diamond cannot possibly contain any double bonds; a combination, say, in the form shown in the figure (see top of next column), with one atom of carbon at each of the six corners, and with each atom connected with its neighbour by a double bond, is altogether impossible.

Imagine, however, at each of the six corners of a regular octahedron, a single molecule of marsh-gas, CH_4 , i.e.,



altogether C_6H_{24} , and then imagine all the 24 hydrogen atoms successively removed, so that each carbon atom is connected with each of its neighbours only by a single bond, and thus all six atoms of carbon are united together in a single whole. Then you obtain, as the most simple representation of the molecule of the diamond, a regular octahedron, with one atom of carbon at each of its six corners, while the edges represent the mutual bonds:—



Several simple molecules of this kind may be combined into one crystallised particle of the spectrochemically normal diamond.

15. Thanks to the explanation of the optical behaviour of benzene, with the resultant discoveries, it all at once became possible to understand the causes of the spectro-chemical abnormality of whole classes of bodies, such as the olefines, diolefines, terpenes, aromatic compounds, &c., and light was cast on the chemical constitution of whole classes of bodies.

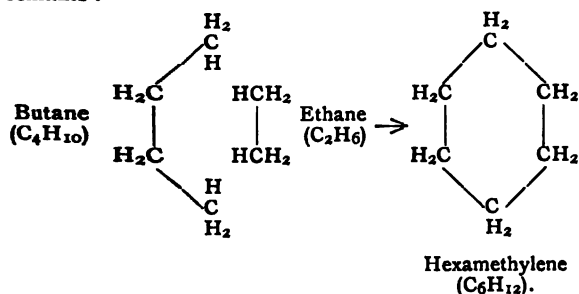
At the same time, however, it at once became apparent why both Landolt and Gladstone had succeeded in observing complete optical normality in very numerous substances of the most various types—alcohols, acids, ethers, hydrocarbons, &c. And now it was understood why in such bodies the molecular refraction is determined solely by the component elements, while the different grouping of the atoms, i.e., the isomerism, remains without any appreciable optical influence.

All the bodies of this kind proved to be either paraffins, i.e., saturated hydrocarbons or simple derivatives of the same. But the paraffins, as we now know, are always optically normal, because they contain no double carbon bonds. For this reason all such simple derivatives of the paraffins must also be normal. Their molecular refraction will thus always correspond to the elements of which they are composed, however the atoms may be grouped, i.e., chemical isomerism is here also without influence.

16. For the same reason, however, all cycloid (ring-shaped) closed formations, if they contain no double carbon bonds, must be optically normal, for those bodies also may be conceived as originating in the simple replacement of hydrogen by paraffin fragments, and may therefore be regarded as combined paraffins.

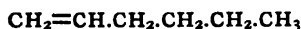
Thus we can imagine the hexamethylene already mentioned not only as formed from hexane by removal of two hydrogen atoms from the ends, but also as arising from ethane and butane, i.e., from two paraffins, by the removal

of four hydrogen atoms and welding together of the remains :—



As a combined paraffin, hexamethylene must be normal, as is also confirmed by experiment, and here we see again, as in the case of the diamond, that a progressive removal of hydrogen and increase of carbon need not lead to the slightest optical anomaly.

At the same time there arises here a case of the optical influence of isomerism, for hexylene, which has already been mentioned, with the same formula (C₆H₁₂) as hexamethylene, but in structure an olefine :—



possesses the familiar refractive increment of 2 units. This example again shows how the spectro-chemical behaviour of a body discloses its chemical structure by enabling us to distinguish with certainty between an optically normal cycloid (or ring-substance), and an isomeric open-chain olefinoid formation, which is optically abnormal.

(To be continued).

THE ISOLATION OF TERBIUM.

By G. URBAIN.

In a previous paper (*Comptes Rendus*, vol. cxxxix., p. 736) I stated that I had just obtained an earth which in solution showed a visible single absorption band, $\lambda = 488$, characteristic of an element which M. Lecoq de Boisbaudran called by the notation Z δ . This earth, which is immediately connected with gadolinium in the series of this rare earths, can be obtained by three distinct methods of fractionation :—(a) Crystallisation of the double nitrates of this earth and nickel, (b) crystallisation of simple nitrates in presence of bismuth nitrate, (c) crystallisation of the ethyl sulphates.

Besides the characteristics of Z δ this earth shows the fluorescence spectrum (inverse spectrum), which M. Lecoq de Boisbaudran attributes to an element, Z β (*Comptes Rendus*, vol. c., p. 1437; 1885, vol. ci., pp. 552, 558; 1886, vol. cii., p. 899), the spark spectrum which Demarcay attributes to an element, Γ (*Comptes Rendus*, 1900, vol. cxxxi., 387), and the phosphorescence spectrum which Sir W. Crookes has attributed both to a meta-element of yttrium and to an element G β .

This earth, however, also contains gadolinium. To completely separate the pure earth from gadolinia, I first fractionated the double nitrate of this earth and nickel; after this, to eliminate the last traces, I further fractionated, on M. Lecoq de Boisbaudran's advice, by means of ammonia, which concentrated the most basic portions in the tail of the fractionation.

I thus obtained about 7 grms. of an earth which, after incessant fractionations for nearly a year, I found to be identical with the experimental definition of the element.

The principal characteristics of this earth, to which the name of terbium may be strictly reserved, are as follows :—

Absorption Spectrum of Neutral Chloride Solution.

λ	
488	The middle point of a diffused band, Z δ , one of the least intense of this spectrum.
382.5—374.9	Diffused band. Faint from 382—379; stronger from 379—375.
371.0—367.7	Diffused band; relatively strong.
361—357.2	Medium; diffused.
354.2—349.6	Diffused double band. Between 354.2 and 352 of mean intensity; from 351.7—349.6 more intense.
343—341	Medium diffused.
340—338.4	"
328.8—324.3	Intense band; very wide and very diffused. The maximum intensity is at 326.
319.2—315.9	Intense, much diffused band.
304.5—301.2	Approximate limits of a generally indistinct band.

The general intensity of this spectrum is faint compared with that of the spectrum of dysprosium, which I intend to describe shortly. The general faintness of the spectrum caused me to doubt for some time the homogeneity of the earth.

The chloride solution gives a reversed, very bright spark, and a beautiful green fluorescence (Z β of M. Lecoq de Boisbaudran).

The pure oxides do not give any visible phosphorescence. The oxide of terbiferous gadolinium gives a green phosphorescence (G β of Sir W. Crookes). A trace of terbium diluted with a considerable mass of alumina gives a magnificent white phosphorescence almost identical with that of a specimen (formed of Z β .O₃.5Al₂O₃), which M. Lecoq de Boisbaudran kindly lent me. This reaction is of a remarkable sensibility.

The line spectrum will be described later.

It contains more than a thousand lines, of which the greater number are faint and often diffused. The eight strongest have been described by Demarcay under the notation Γ .

All these characteristics diminish simultaneously both as the gadolinium and dysprosium ends of the fractionation are approached. The colour of the oxide varies with the conditions of the preparation. The oxalate, when calcined in a muffle furnace, gives an extremely dark brown oxide, whilst the sulphate calcined at 1600° gives a black oxide.

Terbium oxide, when calcined at a high temperature, is unattacked by cold hydrochloric and nitric acids. The action of dilute acids is also very slow even when hot; intermediate colloidal oxides being produced analogous to those which MM. Wyruboff and Verneuil have described for cerium under the name of condensed oxides. Solutions of pure terbium are colourless, and the salts are analogous to those of gadolinium, but are in general a little more soluble.

Terbium sesquioxide is white and not pyrophoric.

The determination of the atomic weight has been effected by the estimation of the water in the hydrated sulphate. M. Wyruboff, who examined a specimen of this salt, found that the crystalline form is the same as that of the octohydrated sulphates of the earths of this series. Taking O = 16, the atomic weight of terbium cannot differ sensibly from 159.2.

Dysprosiferic-terbias, however, have atomic weights often greater than 160.

The proportion of oxygen in the peroxidation has been determined either by reducing the peroxide by means of hydrogen at a red heat or volumetrically by means of iodine solution. The numbers obtained are not constant. They vary between 1.90 and 2.26 per cent of oxygen. The best formula which I have been able to attribute to terbium peroxide is Tb₄O₇, which therefore requires 2.13 per cent of oxygen.

The terbium extracted from xenotime is identical with the terbium extracted from monazite sands. An examination of the arc spectrum by E. Eberhard confirmed these

results. The complete work of this spectroscopist gives a minute description of the yet unknown spectrum of terbium, which element after sixty years has now taken its place among the list of definite elements.—*Comptes Rendus*, cxli., No. 12.

NOTICES OF BOOKS

Smoke Abatement. By WILLIAM NICHOLSON. London: Charles Griffin and Company, Ltd. 1905.

A CONTRIBUTION to the literature dealing with the abatement of the smoke nuisance will always be welcomed, and this particular work contains many useful suggestions. A historical account of the growth of the smoke abatement movement and of the legislation regarding smoke prevention, both in England and abroad, prefaces the discussion of the causes of the nuisance and the various means which have been adopted to do away with it. While the size of the book precludes the possibility of all types of boilers in use being described in it, a useful summary is given of various smoke preventers and fuel savers, and manufacturers and engineers will no doubt gather some useful information from it. The author also discusses the question of stoking, and insists upon the importance of the employment of efficient stokers, whose sole work is firing; it is interesting to notice with regard to the construction of chimneys that the author advocates very decidedly the building of one tall chimney into the flue of which the flues of all the furnaces of the factory lead, although this is a question upon which expert opinion is somewhat divided.

An Introduction to the Study of Colour Phenomena. By JOSEPH W. LOVIBOND. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1905.

IN this work the author elaborates a new colour theory, to which was awarded a silver medal by the International Jury of Awards at the St. Louis Exhibition in 1904. A new system of colour nomenclature is also introduced, which seems likely to meet all requirements, and the explanations of the theory are illustrated by coloured charts. The author's theory is formulated in a code of nine laws governing visual colour phenomena, and is briefly compared with older theories, an account of its application to scientific and industrial investigations being also given.

A Text-book of Chemical Arithmetic. By HORACE L. WELLS, M.A. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

THIS book contains clear explanations of the usual arithmetical problems which the chemist has to solve in order to interpret his results obtained experimentally, an introduction being devoted to methods of approximate multiplication and division, and to the theory of errors, absolute and proportional. A very good collection of problems and examples is given, some of them requiring considerable dexterity for their solution, while others will be within the powers of the less advanced students. These examples appear to have been judiciously selected and to be typical, while the explanations in the text are such as the student of quantitative analysis should be able to understand readily without additional aid. Tables of five figure logarithms are added.

Elementary Chemistry. Part I. By F. R. L. WILSON, M.A., and G. W. HEDLEY, M.A. Oxford: Clarendon Press. 1905.

THE first volume of this work contains a very carefully graduated course of mensuration and elementary physics, forming an excellent introduction to the study of chemistry. The subject is attacked entirely from the experimental point of view, and the authors have adopted the plan of

first introducing a set of preliminary questions on each division of the subject, which the student is to answer from his general knowledge. Then a set of experiments is described, illustrating these questions, while at the end of each chapter another and more advanced set of questions is given, together with a few additional problems. The preliminary questions we should imagine would best be answered orally, and in the hands of a good teacher they should be very useful in bringing out the beginners' ideas. The descriptions of the experimental work appear excellent, the directions being quite explicit enough to ensure no mistakes of manipulation being made. The book can be thoroughly recommended, and will no doubt be appreciated highly by teachers of experimental science.

Introduction to Chemical Analysis. By HUGH C. H. CANDY, B.A., B.Sc., F.I.C. London: J. and A. Churchill. 1905.

IN this work the value of quantitative analysis as mental training is recognised, and the enumeration and description of individual tests are subordinated to general discussions of tables and systems and the principles underlying them. As a result the student who works through the book should acquire a valuable habit of mind, and considerable insight into the reasons for the application of the various tests, while at the same time he will do enough analytical work to prepare him for the Preliminary Scientific Examination of the University of London, or the First Examination of the Conjoint Board. Methods of purifying and preparing substances in the pure state, as well as gravimetric and volumetric analysis, are included; the treatment of quantitative work being, however, very brief, and only useful as an introduction to the study of larger works. The book has many characteristic features which mark it out from similar works, and are all in its favour.

An Elementary Text-book of Inorganic Chemistry By R. LLOYD WHITELEY, F.I.C., F.C.S. London: Methuen and Co. 1905.

THE author of this work has to a certain extent hampered himself by writing up to a syllabus (that of the Board of Education), but at the same time the book has a definite value of its own, quite apart from examination considerations, and it will be found very serviceable for use in schools. The order in which the facts are put before the reader is thoroughly logical, and in some respects suggests the "heuristic" method; thus after introductory chapters on chemical physics, the study of the air is taken up, with special attention to the phenomena of combustion and rusting; then water and its properties are considered, and a section is devoted to the study of common salt and the chlorides. The chapters on chemical theory are introduced relatively late in the book, while full directions, well illustrated by diagrams, are given for the performance of the numerous experiments described. The book contains a large amount of information, judiciously selected and well arranged, and the large collection of questions at the end will be valuable to teachers.

Select Methods in Food Analysis. By HENRY LEFFMANN, A.M., M.D., Ph.D., and WILLIAM BEAM, A.M., M.D., F.I.C. Second Edition. London: Rebman, Ltd. 1905.

THE first edition of this book was accorded a very hearty welcome, and the second edition will be found if anything even more valuable. It contains a good deal of new matter, especially as regards the discussion of polarimetry, new processes for the detection of natural colours used as substitutes for fruit and egg colours, &c. Some paragraphs have been omitted to make room for this new matter, but the general plan of the book remains unaltered, and it excellently fulfils its aim of assisting the analyst in his search for adulterations.

Elektrolytische Versinkung. ("Electrolytic Zinc Plating").
By SHERARD COWPER-COLES. Halle-a-S.: Wilhelm
Knapp. 1905.

THE recent developments in the practice of zinc plating are of sufficient importance to warrant the production of a monograph on the subject, such as this small book, which gives a useful summary of modern improvements in the process which is the basis of all methods of zinc plating. Special attention is paid to the mechanical details, in which respect great strides have been made lately, although much still remains to be done, and there is ample scope for the suggestion of improvements. The preparation of the surface of the substance to be covered with zinc, which has to be very carefully performed, is fully described, and altogether the monograph, which has been translated into German by Dr. Emil Abel, gives a very complete account of this branch of electro-plating.

MISCELLANEOUS.

Preparation of Pure Binoxide of Cerium. Its Reduction by Hydrogen.—R. J. Meyer.—The materials used by the author for his experiments were cerite and (more especially) the monazite sands. For the purpose of purification, the material was transformed into the double nitrate of ammonium and cerium. To free this salt from the small quantities of thorium which might be present, the solution of the double salt was treated with sulphuretted hydrogen, and then with H_2O_2 at 60–70°. The thorium is precipitated and the cerium remains in solution. From this solution it is precipitated in the form of basic acetate according to the method described by R. J. Meyer and Koss (*Berichte*, xxxv., 676). The basic acetate obtained is transformed again into the double nitrate, and this latter purified by crystallisation in nitric acid. By this process it is possible to obtain a binoxide of cerium which is not absolutely white, but very slightly yellow. However, the compound obtained is not chemically pure, for, by the action of sulphuric acid, it gives a white sulphate of cerium, from which may be isolated a compound giving a reddish oxide. The impurity consists apparently of praseodymium and lanthanum. The praseodymium is separated by fractional crystallisation of the sulphates, and accumulates in the end fractions. The lanthanum is eliminated by Drossbach's method (German Patent No. 143,106), which consists of treating the neutral solution of cerium with permanganate of potassium and carbonate of soda until there is a persistent rose colouration; acidulate then with nitric acid, and filter. The precipitate contains the hydrated binoxides of cerium and manganese. It is decomposed by $(CO_2H)_2 + HCl$. The oxalate of cerium remains insoluble, and by calcination gives an oxide absolutely free from lanthanum. The small quantity of manganese which may be retained is eliminated by washing with sulphurous acid and hydrochloric acid. The strong colouration taken by oxide of cerium under the action of heat, whether this operation is carried out in a platinum or porcelain crucible, should be apparently attributed to molecular condensations. Even at a high temperature the oxide does not lose oxygen. The reduction of the binoxide by hydrogen only takes place in the complete absence of air. The loss of oxygen is from 2.31 per cent at a dull red heat, to 2.62 per cent at a bright red, and 2.76 per cent at a yellow heat. The blue-black oxide thus obtained is very oxidisable, and is rapidly transformed in the air into a yellow mass of binoxide. By repeating this reduction and oxidation several times, it is observed that the binoxide formed has a tendency to lose less and less oxygen under the action of heat. Although the composition of the oxide of cerium resulting from the reduction of the binoxide is not yet known exactly, it is quite certain that it does not correspond to the formula of a sesquioxide. —*Zeit. Anorg. Chem.*, xxxvii., pp. 378–393.

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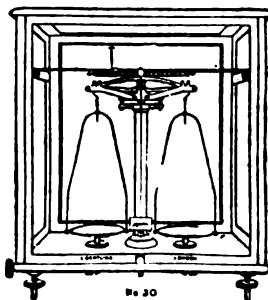
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STUDIES WITH THE LIQUID HYDROGEN AND AIR CALORIMETERS.*

By Sir JAMES DEWAR, M.A., LL.D., Sc.D., F.R.S., Professor of Chemistry at the Royal Institution, and Jacksonian Professor, University of Cambridge.

I. Specific Heats.

THE calorimeter employed in the following researches was similar to that described in my paper on "The Scientific Uses of Liquid Air" (*Proc. Roy. Inst.*, 1894, vol. xiv., p. 398), and in an improved form in Madame Curie's work "Recherches sur les Substances Radio-actives," Second Edition, p. 100. A sketch of the apparatus appears in my paper on "The Absorption and Thermal Evolution of Gases Occluded in Charcoal at Low Temperatures" (*Proc. Roy. Soc.*, 1904, vol. lxxiv., p. 123).

The arrangement employed consists essentially of a large vacuum vessel capable of holding 2 or 3 litres, into which is inserted a smaller vacuum vessel of 25 to 50 c.c. capacity constituting the calorimeter, the latter being sealed on to a long narrow tube which projects from the mouth of the exterior vessel, in which it is lightly held by a loose packing of cotton-wool. A little below the upper end a branch tube is taken off which conveys the volatilised gas from the calorimeter to the gas receiver. To the extremity of the projecting tube a small test-tube, to hold the portions of substance experimented on, is attached by a short piece of rather wide rubber tubing which forms naturally a movable joint that can be bent into any position. With care I have found this valve gives as good results as more elaborate means of securing the dropping of the substances into the calorimeter. A small vacuum vessel containing solid carbonic acid, liquid ethylene, liquid air, &c., into which the test-tube is placed, cools the materials to different temperatures below those of the laboratory, or alternatively it may be heated in the vapour of water or other liquids.

The general constants for liquid gas calorimeters are given in Table I.

Thus an instrument in which liquid air is used has twice the sensibility of a corresponding one in which liquid ethylene is employed, whereas the substitution of liquid hydrogen for liquid air increases the delicacy of the calorimeter some seven times. It is easy to detect the transference of 1/50 of a gramme calorie in the liquid air instrument, whilst 1/300 of a gramme calorie can be similarly observed in the liquid hydrogen form of the calorimeter.

In preparing for use a liquid air calorimeter, some 2 litres of old liquid air containing a high percentage of oxygen are poured into the large vacuum vessel, and the calorimeter, filled with some of the same fluid, is immersed therein. An experiment is conducted by tilting up the little test-tube previously cooled or heated, thereby dropping into the calorimeter a portion of any substance previously weighed. The substance, if left under normal conditions, in this

way falls from the temperature of the room to that of liquid air. The heat given up by it to the liquid air volatilises some of it, which is carried off by the branch tube and measured in a graduated receiver. Immediately preceding or following this observation, a similar experiment is made with a small portion of a selected standard substance, namely, lead. The quantity of lead is so chosen as to produce about the same volume of gas in the receiver as that supplied by the portion of substance experimented on. By this means, the circumstances of the two observations are made as similar as possible, and thereby many sources of error are eliminated.

The handling of the instrument has been carefully studied and improved since the earlier experiments. I find that the vacuum of the calorimeter itself should be a mercury vacuum. Before inserting the calorimeter into the vessel of liquid air, it should have a good deposit of mercury over its surface, obtained by placing a little liquid air in the interior of the calorimeter and allowing it to stand for some time. After a considerable quantity of the liquid air in the calorimeter has been volatilised, the boiling-point of the remaining portion rises slightly above that of the exterior mass of liquid air, and the liquid over which the volatilised gas is collected is apt to "suck back." When this takes place the calorimeter should be emptied and filled anew from the external vessel. The tube coming from the calorimeter ought to be of the size of wide quill tubing, and the free end of the branch tube should be so arranged below the surface of the liquid in the collecting vessel as to produce no resultant pressure. With these precautions it is easy to get results accurate to within 2 per cent.

The use of pure oxygen has no advantage over that of liquid air which has stood for some days, and thus contains a high percentage of oxygen. Pure nitrogen cannot be used without taking special precautions to prevent the atmosphere from getting access to the calorimeter, as otherwise the air liquefies and causes great uncertainty in the working of the instrument.

When liquid hydrogen is similarly used, precautions have to be taken to keep air from getting condensed to the solid state in the neck of the calorimeter. For this purpose, a slow current of dry hydrogen, from an ordinary Kipp apparatus, is kept discharging, partly through the aperture by means of which the bodies fall into the calorimeter, and partly through the tube by which the evaporated hydrogen escapes to the receiver, until everything is ready to make the experiment. The hydrogen is led in by means of a T-shaped piece of tubing, with a stopcock attached, placed between the calorimeter and the gas-collecting receiver.

When the body has to be transferred from solid carbonic acid or liquid air to the calorimeter, the following procedure is adopted:—It is placed in the small test-tube, above the indiarubber joint, which is inserted into a small vacuum vessel containing some of the substance (solid carbonic acid or liquid air), so that at the moment of making the experiment the solid, by a quick vertical movement of the vacuum vessel, is thrown into the calorimeter. A little cotton-wool inserted in the mouth of the vacuum vessel prevents the carbonic acid paste, or liquid air, from being ejected.

Among the sources of error which may occur, the following should be noticed and allowed for. In dropping a small body from the temperature of the laboratory (say)

TABLE I.

Liquid gases.	Boiling-point.	Liquid volume, 1 grm. at boiling-point, in c.c.	Latent heat, in grm.-calories.	Volume of gas at 0° and 760 m.m. per grm.-calorie, in cubic centimetres.
Sulphurous acid	+10°0	0.7	97.0	3.6
Carbonic acid	-78.0	0.65 (solid)	142.4	3.6
Ethylene	-103.0	1.7	119.0	7.0
Oxygen	-182.5	0.9	53.0	13.2
Nitrogen	-195.6	1.3	50.0	15.9
Hydrogen	-252.5	14.3	125.0	88.9

* A Paper read before the Royal Society, June 8, 1905.

TABLE II.

	Number of experiments.	Range of temperature.	Weight, in grms.	Volume of gas in c.c.	Specific heat.
Diamond ..	4	18° to liquid air	1'901	271'5	$S. H. = \frac{1'164}{1'901} \times \frac{271'5}{106} \times 0'0295 = 0'0463.$
Lead ..	2		1'164	106'0	
Diamond ..	2	Solid carbonic to liquid air	1'729	54'0	$S. H. = \frac{0'50}{1'729} \times \frac{54}{23'5} \times 0'029 = 0'0193.$
Lead ..	1		0'500	23'5	
Diamond ..	3	Liquid hydrogen to liquid air	2'142	58'5	$S. H. = \frac{1'996}{2'142} \times \frac{58'5}{351} \times 0'0280 = 0'00435.$
Lead ..	4		1'996	351'0	

TABLE III.—Specific Heats.

Substance.	Number of expts.	Range.	Specific heat.
Diamond	17	Liquid air to 18'5°	0'04727
	8	Liquid air to solid carbonic acid	0'01905
	3	Liquid hydrogen to liquid air	0'00435
Graphite	1	Liquid air to 19'5°	0'0948
	2	Liquid air to solid carbonic acid	0'0599
	2	Liquid hydrogen to liquid air	0'0133
Ice	3	Liquid air to -18°	0'348
	8	Liquid air to solid carbonic acid	0'285
	2	Liquid hydrogen to liquid oxygen	0'146

TABLE IV.

Substance.	18° to -78°.	-78° to -188°.	-188° to -252'5°.
Diamond	0'0794	0'0190	0'0043
Graphite	0'1341	0'0599	0'0133
Ice	0'463*	0'285	0'146

* This is from -18° to -78°.

TABLE V.

Substance.	Range.	Specific heat.
Diamond	-79'7° to +21'4°	0'0806
Graphite	-79'3° to +21'6°	0'1301

TABLE VI.

Number of observations.	Substance.	Weight used, in grms.	Range of temperature, °C.	Volume of gas, in c.c.	Specific heat.
1	German silver	0'22	-18 to -188	48	0'080
1	Brass	0'627	+19'5 -188	166	0'099
1	Brass	0'244	-188 -252'5	66 (H)	0'043
2	Tellurium	0'643	+18'2 -188	99'5	0'047
2	Sulphur	0'289	+18'2 -188	131	0'137
2	Selenium	0'353	+18'2 -188	80	0'068
2	Potassium alum	0'180	+18'8 -188	152'5	0'256
2	Potassium alum	0'376	-78 -188	130	0'223
2	Chromium alum	0'20	+20 -188	162	0'243
2	Chromium alum	0'392	-78 -188	135	0'222
1	Calcium chloride (hydrate)	0'184	+20 -188	180	0'294
1	Calcium chloride (hydrate)	0'336	-78 -188	141	0'271
3	Sodium chloride	0'105	+16 -188	55'2	0'187
2	Sodium chloride	0'253	-78 -188	65'5	0'164
3	Ammonium chloride	0'054	+16 -188	45'8	0'300
2	Ammonium chloride	0'130	-78 -188	42'5	0'207
2	Naphthaline	0'55	+16 -188	31'5	0'202
2	Naphthaline	0'105	+16 -188	57'25	0'194
1	Naphthaline	0'090	+15 -188	50'5	0'204
2	Naphthaline	0'203	-78 -188	40'6	0'126
1	Paraffin	0'08	+15 -188	68'5	0'312
1	Paraffin	0'105	-78 -188	38'5	0'176
1	Silver iodide	0'307	+16 -188	44'5	0'052
2	Silver bromide	0'196	+16 -188	35'5	0'064
2	Silver chloride	0'215	+16 -188	49'75	0'082
5	Solid carbonic acid	0'164	-78 -188	57'1	0'215
1	Solid carbonic acid	0'15	-78 -182'5	50	0'225
1	Solid carbonic acid	0'190	-78 -182'5	62	0'223
2	Solid ammonia	0'14	-103 -188	72'25	0'519
2	Solid ammonia	0'156	-103 -188	77'5	0'490
3	Solid sulphurous acid	0'325	-103 -188	75'2	0'228
3	Solid sulphurous acid	0'311	-103 -182'5	57'3	0'236

into liquid air, the range of temperature through which the body passes in one-third or one-fourth of a second is some 200° . Some of its heat will be lost to the vapour of the gas in the tube before it reaches the liquefied gas; and some at its various impacts on the walls of the glass-tubing, as it passes on to the calorimeter. The consequence of these losses will be to make the quantity of gas measured in the collecting receiver err by defect. Experiments were made with cooled substances to estimate the effect of a similar error in the opposite direction. It was found that 1 grm. of lead, ejected at the temperature of liquid air into the calorimeter filled with liquid air, absorbed enough heat on its passage to produce 1 c.c. of air in the gas receiver; roughly 1 grm. of lead falling through 200° into liquid air produced 100 c.c. of air in the receiver; hence, in this case, the error is within $\frac{1}{2}$ per cent. A similar observation with diamond gave 1.8 c.c. in comparison with 150 c.c.—an error of about $\frac{1}{75}$ per cent; and graphite gave some 4 c.c. in comparison with 300 c.c.—an error of about $\frac{1}{75}$ per cent. Such errors may be neglected in these results.

The observations were reduced by comparison with lead. The method of comparison has obvious advantages. Each day when experiments were being made on any substance, a concomitant series was made on lead, so that unknown errors would affect the results equally, and thus produce volumes of gas in the receiver accurately proportional to the quantities of heat carried into the calorimeter. The choice of the particular metal in question was based on the following considerations:—The low specific heat of lead enabled small quantities of heat to be conveyed into the calorimeter, while the mass of metal was still considerable; the variations in the specific heat of lead with temperature are small, and are very nearly a linear function of the temperature; and, lastly, this metal is easily obtained very pure.

The values taken for the specific heat of lead were:—

		Specific heat.	
Between -252.5° and -188° , or at -220.5°			$= 0.0280$
" -188.0° " -78° " -133.0°			$= 0.0290$
" -188.0° " $+18^{\circ}$ " -85.0°			$= 0.0295$

From calculations based on these values, an error of a degree in the first of these ranges would only affect the specific heat by 0.000006; a similar error in the second range would produce the same variation in the specific heat; and in the third range the variation would be 0.000004. Hence a variation of from 10° to 20° in any of these ranges would not affect the given values of the specific heat noticeably.

As a selection those given in Table II. may be taken as typical of the reduction of the diamond results.

The mean results of the experiments made with diamond, graphite, and ice are given in Table III. In the second column the number of experiments is given; the third column specifies the range of temperature through which the substance fell in giving up its heat at the lower temperature; the fourth column contains the mean specific heat of the substance calculated by comparison with that of lead, each separate experiment being compared with an immediately preceding or succeeding experiment with lead.

From the results given in Table III. are constructed the summary of specific heats stated in Table IV.

It appears from these values that between the ordinary temperature and the boiling-point of hydrogen the specific heat of the diamond has been reduced to $\frac{1}{10}$, whereas under similar conditions graphite has diminished to about $\frac{1}{10}$. Further it will be observed that at the lowest temperatures the specific heat of graphite is about three times that of the diamond. It is also worthy of being recorded that the values of the specific heats of diamond and graphite taken between the temperature of liquid air and boiling hydrogen are far smaller than that of any known solid substance, being even lower than that of any gas taken under constant volume.

Early determinations of the specific heat of carbon in any of its forms showed complete departure from the law

of Dulong and Petit. But all such experiments were in general made over a range of temperature from about the freezing-point of water to some 200° or 300° C. In April, 1872, Professor H. F. Weber read a paper on the specific heat of carbon before the Chemical Society of Berlin. I had made experiments on the same subject for the purposes of a paper read on April 1 of the same year before the Royal Society of Edinburgh, a continuation of which was read to the British Association in the following August. Both of these papers appeared in the *Philosophical Magazine* of 1872 (H. F. Weber, "The Specific Heat of Carbon," *Phil. Mag.*, 1872, Ser. 4, vol. xlv., p. 251; J. Dewar, "The Specific Heat of Carbon at High Temperatures," *Phil. Mag.*, vol. xlv., p. 461).

Professor Weber's observations extended from 0° to 200° , and led him to the conviction "that the specific heat of carbon in all its allotropic modifications varies to a considerable degree with the temperature." This he verified by finding that "the specific heat of the diamond is tripled when the temperature is raised from 0° to 200° ." My own investigations at that time consisted of two groups, the first from 20° to the boiling-point of zinc, taken as 1040° C., and the second to the temperature of the oxy-hydrogen blowpipe, some 2000° C. I found that the mean value of the specific heat of gas-carbon in the first range was 0.32, and for the second range was 0.42, and I added "the true specific heat at 2000° must be at least 0.5; so that at this temperature carbon would agree with the law of Dulong and Petit." In 1875, Professor Weber published results (*Phil. Mag.*, 1875, Ser. 4, vol. xlix., p. 285), proceeding by a series of intermediate steps up to 1000° , and showing finally "that from the point (about 600°) at which the specific heat of carbon ceases to vary with increase of temperature, and becomes comparable with that of other elements, any real difference in the specific heats of the two modifications disappears, and carbon obeys the law of Dulong and Petit."

Professor Weber further showed that the specific heat of carbon, in both its forms, when plotted to temperature as abscissa, produced a curve with a point of inflection in it, like the Old English *f*. He found the point of inflection at about 60° C. for diamond and at about 0° C. for graphite (*Phil. Mag.*, vol. xlix., pp. 180, 279). The results given by Weber lead to Table V.

The close agreement between the result of the present investigation for diamond and Weber's result over the same range is noteworthy; the slight difference in the case of graphite may easily be accounted for by the difference in the graphites used. But in both cases the present results coincide with the trend of the curve as pointed out by Weber for low temperatures. The Weber formula for the diamond, namely,—

$$\text{Specific heat} = 0.0947 + 0.000994t - 0.00000036t^2.$$

if extrapolated would make the specific heat of diamond vanish about -92° C. Behn (*Ann. der Phys.*, 1900, Ser. 4, vol. i., p. 261) gives the specific heat of graphite between -78° and -186° as 0.075, which is much higher than the value given in Table IV.

Previous observations on the specific heat of ice are few, but the following have been noted:—

Regnault	-78° to 0°	0.4627
Person	-30° " 0°	0.505
Person	-21° " -1°	0.5017

These are in agreement with the first result for ice in Table IV.

The specific heat of ice between the temperatures of liquid air and liquid hydrogen has practically been reduced to about one-third the value between 0° and -78° , and has finally only about half the specific heat of steam at constant volume.

It was a matter of some interest to investigate the behaviour of various groups of substances, as regards their specific heats at low temperatures. In Table VI. the specific heats of two alloys are given, which were used in

the course of the present investigation; also those of the group of sulphur, selenium, and tellurium. Two alums, for which Kopp had made some observations, were included in the research, together with three other typical salts. Again, naphthaline and paraffin were a pair, whose specific heats were examined; also the chloride, bromide, and iodide of silver. The results for the solidified gases, carbonic acid, ammonia, sulphurous acid, were of obvious interest, and several observations on them are given. With regard to these bodies, it may be noted that the values found are not far removed from those of the specific heats at constant volume in the gaseous state, and I have no doubt that if the experiments had been extended to temperatures between that of liquid air and hydrogen these results would all have been below the gas constant. The other bodies examined all show diminution of specific heat at the lower temperatures, the most marked examples being the hydrocarbons, paraffin and naphthaline. An almost endless field of research in the determination of specific heats is now opened, in which the use of liquid air and hydrogen calorimeters are certain to become ordinary laboratory instruments.

(To be continued).

THE PRESSURE OF EXPLOSIONS. EXPERIMENTS ON SOLID AND GASEOUS EXPLOSIVES.*

By J. E. PETAVEL.

ALTHOUGH this subject has been dealt with by numerous investigators certain branches of it still remain practically untouched. With regard to the solid explosives used in ballistic work, the maximum pressure developed is usually well known, but the conditions which govern the combustion of the charge and the rate of cooling of the gaseous products require further investigation.

Explosive gaseous mixtures have only been studied at initial pressures but little above that of the atmosphere. Even in the case of coal-gas and air, which forms an exception to this rule, the work has not been extended to high pressures. The present research was undertaken with a view to filling in these gaps.

The first part of the paper describes the apparatus which was used for the investigation of both solid and gaseous explosives; the second part deals specially with the properties of cordite. The pressures are photographically recorded on a revolving cylinder by means of a specially constructed manometer. This manometer was designed with the object of securing the lowest possible time period.

The rise of pressure during the explosion of even the fastest cordite was, by means of this instrument, accurately inscribed without any oscillations being set up in the mechanism of the recorder. The pressures measured range from 100 to 1800 atmospheres (0.7 to 12 tons per square inch).

Many of the results obtained during the study of cordite are most easily expressed graphically, and a study of the curves given in the paper will be found preferable to the most careful abstract. In dealing with such a subject, general statements bereft of the necessary explanations and qualifications are apt to be somewhat misleading.

The present investigation confirms the view that the combustion of cordite proceeds according to parallel surfaces. The rate at which the flame travels towards the centre of each particle of explosive is proportional to the pressure under which combustion is taking place.

This velocity is measured, and it is shown how both the time required to reach the maximum pressure, and also the shape of the curve representing the rise of pressure, may be calculated from the data given.

The effect produced by decreasing the diameter of the explosive is discussed. Though the time required for complete combustion decreases with the diameter, the shape of the curve representing the rise of pressure remains practically unaltered, the scale of time alone being changed. Thus, even were the cordite in the finest state of division, though the combustion would be nearly instantaneous the effect produced would always be distinct from that of a detonation.

The maximum pressures obtained are compared with the measurements made by Noble, with which they are in close agreement. It is shown that the pressure developed by the explosion for various gravimetric densities may be deduced, with a fair degree of approximation, by formulae derived from the kinetic theory of gases. The pressures calculated according to Van der Waals' law are compared with the experimental results.

The modifications introduced by the use of enclosures of different shapes are studied. When the surface of the enclosure is considerable as compared with its volume, the diameter of the cordite has a marked influence on the maximum pressure developed. For large diameters the pressure is considerably below the normal value.

With regard to the rate of cooling the results are compared with those obtained by the author in previous experiments on gases under high pressures (*Phil. Trans.*, A, 1901, vol. cxcvii., pp. 229 to 254). The investigation leads to the conclusion that the rate of cooling depends essentially on the thermal conductivity of the enclosure and not on that of the gas.

With the massive enclosures which are necessary for such experiments, it is found that the rate of cooling varies, not in proportion to the surface, but more nearly as the square of this value. Incidentally, attention is drawn to the very high temperatures which are reached by the inner surface of the steel walls. This throws some light on the important question of erosion.

When the explosion takes place in a long vessel, wave action is frequently set up. A non-uniform distribution of the explosive enhances this phenomenon. The velocity of the pressure-wave is measured and compared with the velocity of sound under similar conditions. Generally speaking, the work confirms the remarkable properties of cordite with regard to its high power and to the regularity of the effects produced.

The paper is accompanied by some 20 figures illustrating the results obtained, and is followed by tables giving the principal numerical values.

A QUICK METHOD FOR THE VALUATION OF FLUOR-SPAR.

By A. W. GREGORY.

THE method of determining the percentage of calcium fluoride present in fluor-spar by calculating from the increase in weight observed when a portion is treated with sulphuric acid and ignited, is unreliable when carbonates and silica are present.

The following modified procedure gives more reliable results, and incidentally the percentage of silica present may be quickly and accurately determined.

The sample is dried at 120° C.

1. Two grms. of the dried sample are then ignited at a red heat until the spar ceases to lose weight.

In most cases this loss in weight represents the CO₂ expelled, with sufficient accuracy for ordinary valuations.

Where great accuracy is required the CO₂ may be estimated by other methods.

2. A 2 gm. portion is treated with pure hydrofluoric acid in a tared platinum dish. After careful evaporation the spar is ignited and weighed. This operation is repeated until a constant weight is obtained.

* Abstract of a Paper communicated to the Royal Society.

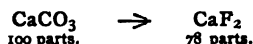
3. A similar weight of the spar is placed in a small platinum dish and tared.

Strong sulphuric acid is added cautiously, evaporated to dryness, and the residue ignited and weighed.

If the quantity of silica is considerable the residue must then be treated with hydrofluoric acid. Finally, however, the spar must be again treated with sulphuric acid and ignited.

The percentage of CO_2 may be calculated from operation No. 1.

In operation No. 2 the calcium carbonate will be converted into fluoride. If silica is entirely absent there will be a loss in weight exactly half of that obtained in operation No. 1; since—



whence the loss is equal to $100 - 78 = 22$ parts. The difference between the actual weight after the operation and the weight which may be deduced from operation No. 1 is equal to the amount of silica present. (When the silica is partly present as silicate this is not strictly true).

In the third operation there is an increase in weight due to the conversion of the calcium carbonate into calcium sulphate and of the fluoride into the same compound; there will also be a loss of any silica present.

The weight of silica obtained in operation No. 2 is added on to the final weighing in operation No. 3, and the increase in weight due to the formation of calcium sulphate from the carbonate subtracted. The remaining increase in weight is due to the conversion of the fluoride into sulphate, from which the percentage of calcium fluoride may be calculated.

THE AVAILABILITY OF MIXED FERTILISERS.

By W. F. SUTHERST, Ph.D., F.I.C.

ONE finds in agricultural practice that mixtures of manures are nearly always more beneficial than the use of, say, one—e.g., superphosphate—and one naturally concludes that it is in the ingredients of the mixed fertilisers that the soil is lacking, and consequently the crops are enabled to grow to greater advantage. According to Liebig's law of minimums, the plant grows in proportion to the ingredient present in the soil in the least quantity, so that phosphoric acid, nitrogen, potash, lime, &c., must be present in proportion found in the ashes of plants to enable the roots to take up their full capacity of inorganic matter.

From some experiments carried out by me, it seems that by mixing certain fertilisers together the availability increases in some cases and decreases in others. For instance, in nitrate of soda and bone flour together, the phosphoric acid in the bone flour is much more soluble in 1 per cent citric acid than when alone; this is also the case, to a less extent, when kainite, salt, &c., are mixed with it. When, however, bone-meal containing still a large quantity of organic matter is treated in the same way, less phosphoric acid is dissolved out than when alone. One might explain this by assuming that bone-meal, when in the soil, undergoes fermentation, by which the phosphoric acid is rendered more soluble, but when quantities of inorganic salts are present this fermentation is prevented.

The method for these experiments was as follows:—One grm. each of bone-meal and bone-flour were mixed with equal amounts of nitrate of soda, sulphate of ammonia, kainite, muriate of potash, &c., and, after moistening with water, allowed to stand about three weeks. At the end of that time the mass was treated with 1 per cent citric acid solution, and the amount of phosphoric acid extracted estimated by the molybdate method. The results obtained are given in the accompanying table.

Mixture.	Amount $\text{Ca}(\text{PO}_4)_2$ dissolved. Per cent.
Bone-meal + muriate of potash	26.54
" kainite	23.99
" salt	25.85
Bone-meal alone	29.06
Bone-flour + sulphate of ammonia	44.51
" muriate of potash	49.06
" kainite	47.97
" common salt	45.30
" nitrate of soda	67.70
" salt + nitrate of soda	44.77
Bone-flour alone	43.45

The Agricultural College, Tamworth.

NOTE ON TRIBO-LUMINESCENCE.

By C. S. STANFORD WEBSTER, F.I.C.

WHEN large crystals of artificially prepared salicylic acid are placed on flannel and crushed against a glass plate in the dark, on viewing it from the other side many brilliant flashes are seen to be emitted. With the natural acid only very few flashes make their appearance. The result is proportionately similar on shaking a little of the substances up violently in a bottle. Both artificial and natural salicylic acid respond to radium more than is usually the case with organic compounds possessing tribo-luminescence of the first order.

A convenient method of examining hard substances, both organic and inorganic, for tribo-luminescence, is to rub them on a sheet of ground-glass, viewing the effect from the smooth side; if the substance cannot be held with the fingers it is best placed on flannel for the purpose. The ground-glass may be advantageously fitted in a wooden frame with a handle, and held like a hand mirror; any of the powdered substance that adheres to the ground surface is easily removed with a wet cloth.

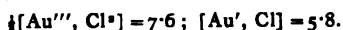
NOTE ON THE CAUSES WHY AN ELEMENT OFTEN PASSES FROM ONE GRADE OF COMBINATION TO ANOTHER WITHOUT GIVING RISE TO INTERMEDIATE COMPOUNDS.

By GEOFFREY MARTIN, B.Sc. (Lond.)

In general, the intensity of the force with which atoms are attracted by an atom A when the latter is in different valency conditions, varies with the particular valency grade assumable by it. Sometimes the intensity of force exerted by A on each individual atom is greatest when A is in a high valency grade; sometimes it is greatest when in a low valency grade. Usually, however, the higher the valency grade which A finds itself in, the feeblér the force it exerts on other atoms. To give one example of this general fact, we will take the case of chromium.

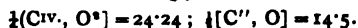
The chromium atom when in an octavalent state (Cr^{VIII}) exerts but a very feeble force on oxygen, CrO_4 evolving O at $20-25^\circ \text{C}$. In a hexavalent condition the force which the Cr atom exerts is considerably greater, CrO_3 evolving O at about 195°C . In a tetravalent condition the attraction which the Cr atoms exert is still greater, CrO_2 evolving O at 300° . Finally, in the trivalent condition the attractive force the Cr atoms exert on the O is enormous— Cr_2O_3 not parting with O even at the highest temperatures. The same phenomena is met with in the case of the majority of elements capable of existing in several valency grades of combination. Did the rule always hold true, it would be invariably easier to detach an atom from a

molecule containing many atoms attached to the central atom A than from one containing only a few atoms attached to A. But this is not always the case; for example, trivalent gold undoubtedly attracts chlorine with a greater force than monovalent gold. Thermal data shows this:—



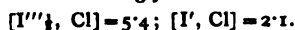
Also the chemical behaviour of AuCl_3 and AuCl leaves no doubt that AuCl_3 is the stabler of the two compounds— AuCl being the easier to decompose both by water and heat.

Similar cases are furnished by indium, In''' exerting a stronger force than In'' and In' , judged from the behaviour of the chlorides, InCl_3 , InCl_2 , InCl . Civ. attracts O and S more strongly than Cii. :—



CS is decomposed into C and S at 200°C ; CS_2 is capable of standing a much higher temperature—showing that Civ. attracts S more strongly than Cii. .

I''' attracts Cl more strongly than I' :—



The compounds of molybdenum, mercury, platinum, and ruthenium furnish further example.

This is the cause why high-grade compounds often decompose discontinuously into low grade compounds without giving rise to intermediate compounds. For example, MoO_3 when reduced by H passes directly into MoO_2 without giving rise to intermediate oxides, such as Mo_2O_5 or Mo_3O_8 . Rogers and Mitchell (*Journ. Am. Chem. Soc.*, 1900, xxii., 350—351) showed that Mo_3O_8 —an oxide intermediate between MoO_3 and MoO_2 —is more easily reduced in H than is MoO_3 or MoO_2 . This shows that $\text{Mo}^{\text{vi.}}$ and $\text{Mo}^{\text{v.}}$ attract O more strongly than $\text{Mo}^{\text{iv.}}$; so that any conditions which bring MoO_3 or MoO_2 to the point of decomposition would already have decomposed Mo_3O_8 . Similarly, MoO_2 when heated in H passes directly into Mo without producing any of the lower oxides, such as Mo_2O_3 , MoO , or Mo_2O . $\text{Mo}^{\text{iv.}}$, in fact, in MoO_3 attracts the O more strongly than the $\text{Mo}^{\text{iii.}}$ or $\text{Mo}^{\text{ii.}}$ attracts it in Mo_2O_3 or MoO , and thus any influence which is capable of tearing away the O from $\text{Mo}^{\text{iv.}}$ in MoO_2 will still more easily remove it from $\text{Mo}^{\text{iii.}}$ or $\text{Mo}^{\text{ii.}}$ when O is not strongly attracted. For a similar reason $\text{Mo}^{\text{iv.}}$ S_2 , when heated in a current of H, is reduced directly to the metal without forming a lower sulphide (Guichard, *Comptes Rendus*, 1899, cxxix., 1239—1242).

Again, I_2O_5 when heated decomposes at 300° directly into I and O without forming lower oxides. The reason, of course, is that the iodine atom when in the pentavalent state attracts the O atoms more strongly than when in a tetrad, triad, or monad state. So that when the temperature is high enough to detach the O from $\text{I}^{\text{v.}}$ in I_2O_5 , it will still more easily detach it from $\text{I}^{\text{iii.}}$ in I_2O_3 , or $\text{I}^{\text{ii.}}$ in I_2O . So that I_2O_5 passes directly into I and O without giving rise to I_2O_3 or I_2O . In fact, I_2O_5 decomposes at over 300°C , IO_2 at 170° , I_2O_3 at 125 — 130° (Watts' "Dict. of Chemistry," 1897, iii., 18); I_2O_4 is undecomposed by boiling water, whereas both IO_2 and I_2O_3 are decomposed. Similarly, CS_2 goes directly into C and S without giving CS.

The oxides of potassium, K_2O , KO , K_2O_3 , and KO_2 , and of chlorine, Cl_2O , Cl_2O_3 , ClO_2 , Cl_2O_7 , furnish similar phenomena.

As regards stability, the compounds of an element usually separate out into two groups—those of an odd grade of valency and those of an even. So that, in general, in the case of some elements (the so-called "artidiads"), the compounds of an odd type of combination are more stable than the compounds of an even type, whereas in the case of other elements (the so-called "perissads") the compounds of an even type are more stable than the compounds of an odd type.

Sometimes, indeed, so widely do these two classes of compounds differ for one and the same element, that while

representatives of the one class are known, representatives of the other are completely wanting. For example, no monovalent, trivalent, or pentavalent compounds of carbon are known, although divalent and tetravalent (CO , CS ; CO_2 , CS_2) are well known.

Again, the halogens produce monovalent (ClK), trivalent (I_2O_3), pentavalent (I_2O_5) and heptavalent compounds (Cl_2O_7)—all artiad bodies—but the intermediate perissad compounds have not been obtained. Usually, however, representatives of both classes are known; indeed, in the case of Mo and W the perissad and artiad compounds seem to be of nearly an equal degree of stability.

The whole phenomena arises out of the fact (due to an unknown cause) that the intensity of the force with which atoms are attracted by an atom A when in the grades of valence n , $n-2$, $n-4$, $n-6$, &c., are usually greater each to each, than the intensity of force with which it attracts atoms when in the intermediate grades of valence $n-1$, $n-3$, $n-5$, $n-7$, &c. So that the atom will pass directly from the grade of combination n to the grade $n-2$, $n-4$, &c., without producing the intermediate compounds of grade $n-1$, $n-3$, &c.

Of course all this holds only at normal temperatures; at high temperature the element may be most stable as perissad, although at ordinary temperatures it is most stable as artiad; e.g., FeCl_3 and Fe_2O_3 are ordinary temperatures, are more stable than FeCl_2 and FeO ; but at a very high temperature FeCl_2 and FeO are more stable than FeCl_3 and Fe_2O_3 .

These examples I think throw light on the cause why an element does not give rise at a given temperature to compounds of every valency grade, but only to those of certain particular valency states.

I have long convinced myself by the study, extending over years, of the data relating to rare and imperfectly known compounds of elements, that every element is capable of giving rise to valency compounds of every grade between 1 and 8, but owing to the stronger attraction the elements, when in certain valency grades, exert on other atoms, most of these compounds at once spontaneously pass over into these stabler grades of union, and that the unstable grades of union are only revealable to us by accidental influences—such as the immersion of an element in a suitable medium, by altering the temperature and pressure under which we view the elements, &c.

By altering in a suitable manner the external conditions under which we view the element (such as the temperature, pressure, medium in which the element is immersed, and so on) we could probably cause an element to generate compounds of any valency grade.

Indeed, we may safely conclude that the unknown (because unstable) compounds which an element produces are enormously more numerous than the known (because stable). We are, in fact, only acquainted with a few compounds of an element whose stability under ordinary conditions of temperatures and pressure rises above a definite limit which enables them to exist unchanged for a time long enough for us to examine them chemically. The far greater multitude of unstable compounds remain completely unknown on account of the rapidity with which they go over into more stable forms of union. It is only the slow rate of change of the unstable into the more stable forms which enables such an enormous number of carbon compounds to exist simultaneously at ordinary temperatures in a state of very slow change. At a red or white heat the rate of change is so greatly increased that nearly the whole of organic chemistry is destroyed, and carbon then behaves like other elements in its capacity of giving only a few compounds of greater stability. If by any means, in the case of a given element, we could arrest or greatly diminish this rate of change of the unstable compounds into stable compounds, we would find the element produced compounds whose range and multitude rivalled those of the carbon compounds at ordinary temperatures. Perhaps low temperatures will give us this means.

This and other matters relating to affinity are discussed

in my work, "Researches on the Affinities of the Elements" (London, Macmillan and Co., 1905), to which for further information the reader is referred.

University of Kiel.

THE DEVELOPMENT OF SPECTRO-CHEMISTRY.*

By Professor JULIUS WILHELM BRÜHL, Ph.D., Sc.D.,
Hon. Mem. R.I., Professor in the University of Heidelberg.

(Concluded from p. 177).

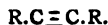
VI.

17. CARBON can thus act variously upon light according to the manner in which its atoms are combined. We can therefore transfer the refractive increment of the double bond to the atom itself.

In the diamond, and in all paraffinoid carbon compounds, the atomic refraction of carbon equals 5; it is therefore equal to 10 for two carbon atoms. The double bond increases the refraction by 2, so that for two carbon atoms with a double bond the refraction amounts to 12. The atomic refraction of one carbon atom with a double bond is therefore equal to 6, i.e., 20 per cent greater than that of the atom with the single bond:—

	Atomic refraction.
One carbon atom C (diamond and paraffins) . .	5
Two carbon atoms 2C (diamond and paraffins) . .	10
Double bond	2
Two carbon atoms with a double bond $C=C$. .	12
One carbon atom with a double bond $C=$. .	6

18. Carbon, being a quadrivalent element, can also appear with triple bonds:—



Experiment has shown that carbon with a triple bond also acquires a special atomic refraction.

Thus it becomes possible to establish the presence of this kind of bond in substances, and to distinguish it from the double and simple bonds—a further criterion of structure.

19. In consequence of these discoveries it became highly probable that all multivalent elements, such as carbon, possessed an atomic refraction varying with the kind of bond, while the univalent elements, such as hydrogen, display constant optic values, because atoms such as theirs can only be linked with a simple bond.

Later researches have confirmed this. The univalent halogens give, like hydrogen, constant atomic refractions, both in the elementary state and in their compounds. The multivalent elements, on the other hand, such as oxygen and nitrogen, display different optical values, according to the kind of bond.

In the course of such researches the behaviour of oxygen as a quadrivalent element, which had been previously conjectured, was established with certainty, and afterwards confirmed synthetically by Collie, Tickle, and others.

20. The theory which accounted for the optical abnormalities of certain classes of bodies, making them, in fact, abnormalities no longer, has proved extraordinarily fruitful. It formed the starting-point of all subsequent discoveries in the subject, and, indeed, we may describe the progress of this branch of science during the last twenty-five years as based essentially on this conception.

For not until we had fathomed the mystery of the benzene refractive increment 6, was it possible to know for certain that the variable valency of the multivalent elements is always of determining influence on the optical behaviour of bodies. Thus for the first time a spectrochemical method was called into being for the study of chemical structure,

and the foundations were laid of what we now call "Spectro-chemistry."

VII.

21. We must now return once more to the formula for refractivity. Newton's expression $\left(\frac{n^2-1}{d}\right)P$ had proved not constant for the temperature in the case of fluid bodies, and was therefore replaced by Gladstone and Dale's more satisfactory ratio $\left(\frac{n-1}{d}\right)P$. For twenty years and more this did admirable service. As, however, the number of observations kept on increasing, even this formula betrayed imperfections which finally led to its abandonment. It is impossible here to follow the argument in detail, and we must be content with the remark that comparisons of bodies in different states of aggregation failed to yield satisfactory constants. The values of $\left(\frac{n-1}{d}\right)P$ for a fluid or solid substance always came out considerably greater than for the same substance in the state of gas or vapour.

22. Then by a happy chance two physicists, L. Lorenz, of Copenhagen, and H. A. Lorentz, of Leyden, came forward simultaneously in 1880 with a new expression for refraction. One of them started from the ordinary theory of light, the other from Maxwell's electromagnetic theory of light based on Faraday's views, and they both reached the same result, viz., that the true measure of refractivity is furnished by the expression—

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{P}{d}.$$

Experimental tests showed that this theoretical expression was in fact, for all bodies, practically unaffected not only by temperature and pressure, but also by the state of aggregation.

Chemical tests confirmed the utility of the new optical standard, since the operation of all the laws before mentioned was observed to be even more exact when the new constant was applied.

23. Moreover, the expression for refraction proved valuable in another respect. It was found to be very suitable for measuring the dispersive power of bodies.

If n_v and n_r denote the refractive indices for the limits of the visible spectrum, i.e., for violet and for red light, the difference of the refractivities for these end-rays of the spectrum:—

$$\left(\frac{n_v^2-1}{n_v^2+2} - \frac{n_r^2-1}{n_r^2+2}\right)\frac{P}{d}$$

is the measure of the power of different bodies to disperse light—to broaden out the spectrum. This ratio proved to be constant as regards temperature, pressure, and state of aggregation.

Gladstone had already observed that dispersion, like refraction, was connected with the chemical nature of bodies. Quantitative relations were, however, only obtained when a constant for refractivity had been found. And then from the molecular dispersions of compounds the atomic dispersions of their elements were deduced.

We cannot enter here into the relations which were thus shown to exist between the chemical composition of substances and their power to disperse light. We need only remark that the case as a whole is analogous to that of refraction. Dispersion is, however, a still more sensitive and more constitutional property, and therefore in many cases it is specially adapted as an aid to research on chemical structure.

VIII.

24. It only remains to add a few remarks on the applications of spectro-chemistry in science and in practical life.

I have already shown the principles on which spectrochemical methods of examination in general can be applied to the solution of scientific problems, to the discovery of

* A Lecture delivered at the Royal Institution, May 26, 1905.

the chemical structure of single substances or whole classes of bodies.

Now there are a large number of substances, some of them artificially built up by synthesis out of their elements, some of them occurring in the vegetable and animal kingdoms, or even in inorganic nature, the structure of which is of remarkable delicacy and instability. Among them are, for instance, the so-called "tautomeric" compounds, hydrogen peroxide, and many other unstable compounds. Substances of this kind are of a very special interest, for in consequence of their tendency to change, they are the principal cause of metamorphoses, the unceasing circulation of matter, the eternal birth and decay that goes on in nature.

Research into the atomic structure of such bodies by purely chemical methods is often very difficult, and not seldom impossible, because, owing to their sensitive organisation, chemical interference leads either to changes in the grouping of the atoms, which cannot always be controlled, or even to total decomposition.

In such cases it is of course of the greatest value to be able to examine the constitution of the bodies without affecting them chemically; and spectrochemistry, as we have seen, gives us the means of doing so. By observing the behaviour of light on its passage through the various substances, we gain an insight into their structure without in any way disturbing it.

25. In the last ten years the spectro-chemistry of the nitrogen compounds has also made remarkable progress. Nitrogen is of the greatest importance as an essential constituent of the proteids, the alkaloids, and many other animal and vegetable products. But its high valency and the extraordinary variety of combinations into which it can enter with other elements, surround it with special complications. Regardless of these, however, the spectro-chemical examination of nitrogen compounds has already yielded useful results, especially in the study of the alkaloids. It is to be expected that this optical method will also be of use in the chemistry of the albuminoids, the study of which is now being prosecuted with so much vigour.

26. One class of substances of increasing importance both to science and to chemical industry is that constituted by the natural and artificial perfumes. An overwhelming majority of them consists of derivatives of the terpenes. We have already mentioned that Gladstone, in this subject also a pioneer, was the first to study the optical behaviour of the terpenes. Since then the explanation of the structure of these bodies and of a large number of rich natural perfumes derivable therefrom has been rendered easier by the use of spectro-chemical methods. Similar assistance has been rendered to the synthetic preparation of valuable scents, such as ionone, the artificial scent of violets. In every scientific laboratory and in every rationally conducted chemical factory where work is being done on perfumes, the spectrometer is now an indispensable testing instrument, and hence also an implement in industrial production.

IX.

27. When scientific research opens up new methods of observing nature, it is generally not long before a use is found for these methods in practical life. The need is soon felt of perfecting, and at the same time simplifying, the scientific apparatus. Efforts in this direction have not been wanting in the case of the spectrometer, and they have been crowned with the most brilliant success.

Professor Abbe, the distinguished physicist who died not long ago, and after him Dr. Pulfrich, constructed spectrometers on the principle of total reflection. These instruments are distinguished from those formerly in use by their extraordinary simplicity and convenience, and they allow also of much more rapid work.

Such instruments, known as total-reflectometers, have been made for the most exact scientific measurements, and also for medical and technical purposes. Special forms are in use for the examination of fats and oils, milk and

butter; to determine the amount of salt contained in salt solutions; the amount of alcohol and extractive matter in beer; for the examination of blood and albuminoids in pathological fluids, &c. Several of these ingeniously contrived instruments give not only the refractive index and the dispersion of a substance immediately, without any calculation, but also directly the percentage of dissolved matter, *e.g.*, of alcohol and extractives in beer.

A number of such instruments from the celebrated factory of Carl Zeiss, of Jena, are here exhibited at my request.

I have now reached the end of my remarks. I have reviewed the development of spectro-chemical research since Newton's time, and we have seen that, although different nations have taken part in the work, a specially large share has fallen to British investigators. For this reason, as I said at the beginning of my discourse, it has been a special pleasure to me to be able to treat of such a subject before the Royal Institution.

There is a saying of Montesquieu's which I venture to hope has its application to this evening:—"Quand vous traitez un sujet, il n'est pas nécessaire de l'épuiser, il suffit de faire penser."

From Newton to our own day—a length of time which our planet takes to complete 250 revolutions round the sun—that is the period through which we have sped in sixty minutes. It will be readily understood that on such a rapid trip we have only been able to stop at one or two view-points, and have been obliged to content ourselves with a hasty survey. I thank you all for having ventured yourselves with me on such a hurried excursion, and I shall be happy if it has been conducted without mishap.

THE ESTIMATION OF SULPHITES BY IODINE.

By R. HARMAN ASHLEY.

VOLHARD's method for the determination of sulphur dioxide and sulphites is accurate and reliable, but involves the inconvenience of making up every solution to be examined accurately to a standard volume of which portions are to be drawn from a burette and made to react with definite amounts of a standardised solution of iodine. The method consists in running the unknown sulphite or sulphurous acid solution into a known amount of a standardised solution of iodine, acidified with hydrochloric acid, to the disappearance of the iodine reaction with starch. This procedure rests upon the facts that the oxidation of sulphite is brought about in the acidified solution, and that, as Bunsen showed, no more than a small proportion of hydriodic acid should be present at the point at which the bodies are made to react. The reaction for the oxidation of sulphur dioxide proceeds normally in dilute solutions according to the equation $2\text{SO}_2 + 2\text{I}_2 + 4\text{H}_2\text{O} = 4\text{HI} + 2\text{H}_2\text{SO}_4$. In solutions too concentrated, however, the secondary reaction, $\text{SO}_2 + 4\text{HI} = 2\text{I}_2 + 2\text{H}_2\text{O} + \text{S}$, takes place, as Volhard has shown, and vitiates the indications (*Ann. Chem.*, cxxlii., 93).

To avoid the inconvenience of the Volhard method it has been proposed by Rupp to bring about the oxidation of sulphites by treatment with an excess of standardised iodine in a solution made alkaline by acid sodium carbonate, and then, after fifteen minutes, to titrate the excess of iodine by sodium thiosulphate (*Ber.*, xxxv., 3694). This procedure, however, is, as has been shown by Ruff and Jaroch (*Ber.*, xxxviii., 409) and by the present writer (*Am. Journ. Sci.*, xiv., 237), faulty in principle and practice, and gives correct results only by a chance balancing of opposing errors. Theoretically it might be possible to overcome the difficulties by treating with acid the alkaline mixture of iodine and sulphite and acid sodium carbonate before attempting to titrate by sodium thiosulphate the excess of iodine.

In the experiments recorded in the table the following

procedure was followed:—The sulphite was treated with 1 grm. of acid sodium carbonate and an excess of standardised iodine solution. The solution was then acidulated with a safe amount of hydrochloric acid, it having been found by experiment that the presence of 10 c.c. of 1 : 4 hydrochloric acid in 125 c.c. of water was without effect upon the determination of iodine by sodium thiosulphate. The excess of iodine after acidification was titrated by standardised sodium thiosulphate. It will be noticed that, in the experiments recorded under A of the table, the excess of iodine used was small, and in these experiments large negative errors are obtained; while in the experiments recorded under B, in which a large excess of iodine was employed, the results are better. They are best when at least twice as much iodine is added as is theoretically required to oxidise the sulphur dioxide. The length of time during which the iodine may act does not affect the results to any very marked degree.

Iodine value of SO ₂ taken. Grm.	Iodine taken. Grm.	Iodine value of Na ₂ S ₂ O ₃ used. Grm.	Error in terms of—		Excess of HCl (1 : 4). C.c.	Vol. at titra- tion. C.c.
			Iodine. Grm.	SO ₂ . Grm.		
A.						
0.2197	0.3143	0.0978	-0.0032	-0.0008	7.5	125
0.2197	0.3143	0.0965	-0.0019	-0.0005	7.5	125
0.2197	0.3143	0.0970	-0.0024	-0.0006	7.5	125
0.1535	0.1913	0.0464	-0.0086	-0.0022	7.5	125
0.1535	0.1913	0.0467	-0.0089	-0.0022	7.5	125
0.1535	0.1913	0.0472	-0.0094	-0.0024	7.5	125
0.1535	0.1913	0.0465	-0.0087	-0.0022	7.5	125
0.2366	0.3194	0.0903	-0.0075	-0.0019	7.5	125
0.2906	0.3825	0.1132	-0.0213	-0.0054	7.5	125
0.3825	0.4463	0.0750	-0.0112	-0.0028	7.5	125

B.

0.1143	0.3143	0.1990	+0.0010	+0.0003	5.0	125
0.1143	0.3143	0.1982	+0.0018	+0.0004	5.0	125
0.1143	0.3143	0.1992	+0.0008	+0.0002	5.0	125
0.1143	0.3143	0.1986	+0.0014	+0.0003	5.0	125
0.1482	0.3187	0.1708	-0.0003	-0.0001	7.5	125
0.1576	0.3187	0.1586	+0.0025	+0.0006	7.5	125
0.1576	0.3187	0.1643	-0.0032	-0.0008	7.5	125
0.1576	0.3187	0.1598	+0.0013	+0.0003	7.5	125
0.1576	0.3187	0.1606	+0.0005	+0.0001	7.5	125
0.1576	0.3187	0.1602	+0.0009	+0.0002	7.5	125
0.1576	0.3187	0.1622	-0.0011	-0.0003	7.5	125
0.1560	0.3195	0.1660	-0.0025	-0.0006	7.5	125
0.1992	0.4460	0.2482	-0.0014	-0.0003	7.5	125
0.1915	0.3825	0.1919	+0.0009	-0.0002	7.5	125
0.2056	0.3771	0.1701	+0.0014	+0.0003	7.5	125
0.2056	0.3771	0.1697	+0.0018	+0.0004	7.5	125
0.2056	0.3771	0.1707	+0.0008	+0.0002	7.5	125
0.2056	0.3771	0.1709	+0.0006	+0.0002	7.5	125
0.2131	0.4470	0.2412	-0.0073	-0.0018	7.5	125
0.2354	0.3825	0.1490	-0.0019	-0.0005	7.5	125
0.2597	0.4463	0.1869	-0.0003	-0.0001	7.5	125
0.2638	0.4463	0.1847	-0.0022	-0.0005	7.5	125
0.2908	0.6375	0.3505	-0.0038	-0.0009	7.5	125
0.3187	0.4463	0.1326	+0.0050	+0.0012	7.5	125
0.3395	0.6275	0.2842	+0.0038	+0.0009	7.5	125
0.3395	0.6275	0.2852	+0.0028	+0.0007	7.5	125
0.3395	0.6275	0.2844	+0.0036	+0.0009	7.5	125
0.3395	0.6275	0.2855	+0.0025	+0.0006	7.5	125

Ruff and Jaroch (*loc. cit.*) take the ground that, in the favourable results occasionally obtained by Rupp's process, an error due to the over-oxidation of the tetrathionate normally formed in the action of sodium thiosulphate upon the residual iodine is apparently balanced by some oxidation of sulphur dioxide by dissolved air, the iodine in solution acting catalytically as well as directly. The theory, however, is quite at variance with the evidence supplied in the table; for, if it were true, under no conditions could iodine in the presence of air act as a correct measure of sulphur dioxide, as it apparently does when used in a

sufficiently large excess; nor does the theory of the catalytic action of iodine explain the fact that when a greater mass of iodine is used, under conditions otherwise similar, we get a larger oxidation of sulphur dioxide.

The most obvious explanation is that, at a low concentration of iodine, an intermediate oxidation product may be formed, and that the formation of this product may be prevented by sufficient concentration of the iodine. It is not unreasonable to suppose that the formation of a small amount of dithionate instead of sulphate is the occasion of the deficient expenditure of iodine noted when the concentration of this element is low, and that the dithionate is not formed appreciably when the iodine concentration is high. The dithionate once formed is but slowly attacked by iodine, and that is apparently the reason why long standing of the mixtures containing a small proportion of iodine does not result in complete oxidation of the sulphite to sulphate. From these considerations, it will be seen that the secondary error of Rupp's process may very probably be due to the formation of some dithionate from the sulphite where the concentration of the iodine is low.

The practical estimation of sulphurous acid or a soluble sulphite may, then, be accomplished with a reasonable degree of accuracy by adding to the solution of the substance, not exceeding 100 c.c. in volume and containing a grm. of acid sodium carbonate, at least twice as much iodine as is theoretically necessary to effect oxidation, acidifying cautiously with hydrochloric acid, and determining with standard sodium thiosulphate the excess of iodine remaining in the acidified solution.

The author takes this occasion to thank Prof. F. A. Gooch for much kind assistance.—*American Journal of Science*, vol. xx., p. 13.

NOTICES OF BOOKS

Chemistry for Engineers and Manufacturers. By BERTRAM BLOUNT, F.I.C., and A. G. BLOXAM, F.I.C. Vol. II. London: Charles Griffin and Company, Ltd. 1905.

THE second volume of this work deals with the chemistry of manufacturing processes, and gives a good review of the general principles underlying the most important chemical industries. The book has been carefully revised for the second edition, and a large amount of new and valuable matter has been added, but otherwise its general scope and scheme have been retained. It will be found a useful and practical book of reference, especially for chemical engineers.

Second Year Chemistry. By EDWARD HART, Ph.D. Easton, Pa.: The Chemical Publishing Co. 1905.

THE order in which the subjects are treated in this book is a serious defect, and one which will undoubtedly restrict its use in this country. Thus, after introductory chapters on molecules and atoms and the properties of gases, gas analysis is taken up, and then dissociation in solutions and electrolysis are discussed. Chapters then follow on the chemical balance, and very brief courses of volumetric and gravimetric analysis are introduced. Schemes for the detection and separation of the non-metals and metals are then given, a return being finally made to quantitative work in a few technical analyses. Although most teachers will agree with the author in recognising the importance of giving the beginner some practice in quantitative work before he proceeds to qualitative analysis, the method he has adopted to attain this object does not seem likely to lead to success. The early performance of simple quantitative estimations undoubtedly impresses upon the student the necessity for care in working, and has an important influence upon his later work in analysis, but it would not appear advisable to begin with gas analysis, which is better postponed until considerable dexterity in quantitative work has been acquired. As for the text, the directions for the

experiments are clearly expressed and the methods appear to be well chosen. The chapter on chemical arithmetic gives very briefly the essentials of the subject, and a collection of examples for working is added, while general questions are interspersed throughout the text.

Kristallinische Flüssigkeiten und Flüssige Kristalle. ("Crystalline Liquids and Liquid Crystals"). By Dr. RUDOLF SCHENCK. Leipzig: Wilhelm Engelmann. 1905.

In Lehmann's work on liquid crystals the investigation of doubly refracting liquids under the microscope is discussed at great length, but the physico-chemical aspects of the investigations are only briefly alluded to; this book, on the other hand, describes the author's quantitative measurements of anisotropic liquids, and may thus be regarded as a supplement to Lehmann's larger work. The author gives an account of the preparation and properties of his material, and the investigation of the properties of the melting- and clearing-points, and has also collected a large number of measurements relating to viscosity, molecular surface energy, specific heat, and dielectric constants; from these measurements important conclusions can be drawn regarding the nature of crystalline liquids. For the sake of completeness, and to give the reader some insight into the optical behaviour and structure of anisotropic liquids, a short account of Lehmann's work is also included.

Thermodynamik Technischer Gasreaktionen. ("The Thermodynamics of Technical Gas Reactions"). By Dr. F. HABER. München and Berlin: R. Oldenbourg. 1905.

This book is written from a somewhat novel point of view; it does not aim at providing a complete treatise of thermodynamics, but at expounding the subject from a technical point of view, constant reference being made to technical examples. While a knowledge of chemistry and technology is presupposed, the amount of mathematics introduced into the text is reduced to the lowest limit possible. The work is in the form of seven lectures, in which the theory of thermodynamics, based upon the method developed by Helmholtz, is considered in detail; starting from elementary notions concerning the latent heat of chemical transformations, the reader passes by easy stages to the more difficult conception of the meaning of entropy, and thereafter to the practical application of the relations deduced from theoretical considerations. One lecture is devoted to a description of methods of determining the specific heats of gases and of the experiments performed by many investigators in this field, while the last lecture deals with relations which are of importance in determining gas equilibria, especially at high temperatures. The addition of a good index would be a great boon to those who use the book.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 11, September 11, 1905.

This number contains no chemical matter.

No. 12, September 18.

The Isolation of Terbium.—G. Urbain.—Inserted in full.

No. 13, September 25.

This number contains no chemical matter.

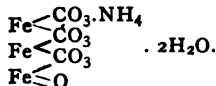
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 12, 1905.

Sulphammonium and its Relations to Nitrogen Sulphide.—Otto Ruff and Emil Geisel.—When sulphur is dissolved in liquid ammonia a blue liquid containing sulphammonium is formed. Moissan has shown that this liquid is not a simple solution of sulphur, but that a chemical compound is formed, to which he ascribed the formula $(\text{NH}_3)_2\text{S}(\text{NH}_3)_2$ or $(\text{NH}_3)_2\text{S}(\text{NH}_3)$. The authors have found that a reversible reaction occurs, as represented by the equation $10\text{S} + 4\text{NH}_3 \rightleftharpoons 6\text{SH}_2 + \text{N}_4\text{S}_4$. The sulphuretted hydrogen formed may be precipitated with silver iodide, and from the residue nitrogen sulphide may be obtained, and thus a new synthesis of the latter is afforded. If a solution of nitrogen sulphide in liquid ammonia is treated with sulphuretted hydrogen the reverse reaction occurs. It is noticeable that in this case, although the solution contains dissolved sulphur, it is not blue but yellowish red. This is due to the presence of excess of ammonium sulphide, which decolourises the solution, dissolving the sulphur to polysulphides. The purplish blue colour of the solution of sulphammonium is probably due to a colloidal solution of elementary sulphur in ammonia and to the products forming during the reaction between sulphur and ammonia. The dichroism of sulphammonium is also possibly an argument in favour of the colloidal nature of the dissolved sulphur, although this same property has also been observed in the case of a number of other solutions which are probably not colloidal.

Organo-metallic Compounds.—Iwan Shukoff.—Diethyl thallium chloride, $\text{Ti}(\text{C}_2\text{H}_5)_2\text{Cl}$, is a strong electrolyte, which, however, in a high state of dilution may be hydrolysed to an appreciable extent. When a solution of $\text{Ti}(\text{C}_2\text{H}_5)_2\text{Cl}$ is electrolysed between two platinum electrodes, at the cathode metallic thallium is separated in crystals, and a gas is given off. It was therefore concluded that thallium ions are present as well as organo-metallic cations, and are formed from them by dissociation. From potential measurements it was found that the concentration of the thallium ions would work out to $10^{-2.07}$ for 0.0161N TiCl , and to $10^{-2.78}$ for 0.0161N $\text{Ti}(\text{C}_2\text{H}_5)_2\text{Cl}$, if Nernst's formula for the system $\text{Ti-meth.}-\text{Ti-salt}$ solution is assumed to hold good, which, however, is not certain. Thus from the potential measurements the only conclusion that can be drawn is that the monovalent thallium alkyl cation acts like a complex ion, which separates off Ti ions to about $1/300$ of its concentration. As regards the gaseous product of dissociation, it was found that it burns with a luminous flame, and consists of a mixture, in which about 15 per cent of unsaturated hydrocarbons may be detected by absorption with bromine water.

New Class of Iron Compounds.—Otto Hauser.—Some iron salts (both ferrous and ferric) are fairly easily soluble in excess of ammonium carbonate solution. From ferrous salts under suitable conditions an iron ammonium carbonate of the formula $\text{Fe}^{2+}(\text{NH}_4)(\text{CO}_3)_2\text{Fe}^{3+}0.2\text{H}_2\text{O}$ can be obtained, and this represents a new type of iron compounds. When excess of ammonium carbonate is added to a solution of a ferric salt, a red precipitate is first formed, and dissolves to a blood-red liquid, in which the iron may be precipitated by $-\text{SH}'$, by calcium chloride, and by boiling with alkalis, but not by a specific ferric ion reagent, such as potassium ferrocyanide. Ammonium carbonate dissolves Prussian-blue, giving a violet-red solution. The iron in such solutions is present as a complex ion. On evaporation, even slowly in the cold, the ferri-ammonium carbonate solution deposits ferric hydroxide, but in closed vessels it will remain unaltered for weeks. The precipitate formed in solutions of ferrous salts by means of ammonium carbonate is more difficultly soluble in excess of the reagent, the solutions being nearly or quite colourless when freshly prepared. They absorb oxygen from the air, and then deposit nearly all their iron in the form of a difficultly soluble greenish white precipitate. This precipitate appears under the microscope to consist of small

double refracting prisms, often forming star-shaped masses. These crystals rapidly darken in air; in dilute acids they dissolve, giving off carbon dioxide, and forming yellowish green solutions. Alkalis separate from them a black strongly magnetic ferroso-ferric oxide, ammonia being given off. Thus the salt is a basic ferri-ferro-ammonium carbonate of formula $\text{Fe}_2^{II}(\text{NH}_4)(\text{CO}_3)_3\text{Fe}^{III}\text{O} \cdot 2\text{H}_2\text{O}$. The constitutional formula appears to be—



It is noteworthy that all the ammonia determinations gave too low a value for ammonia; this is probably due to incipient dissociation. Slow oxidation of the salt gives an olive-green powder in which the proportion $\text{Fe}^{II} : \text{Fe}^{III}$ is 1 : 1, but the author has not yet determined whether this is a single salt.

Phosphorus Pentasulphide.—Alfred Stock and Kurt Thiel.—If white phosphorus, sulphur, and a little iodine are dissolved in carbon disulphide, the solution filtered and heated for twelve hours to 120° — 130° in a steel tube, crystals of phosphorus pentasulphide are obtained, which may be purified from traces of sulphur, iodine, and iron by Hofmann and Stock's method (*Berichte*, 1903, xxxvi., 314). Stock and v. Schönthan noticed that the greater part of the pentasulphide thus prepared melts at 255° , while the melting-point of ordinary phosphorus pentasulphide is 275° — 276° . Hence they concluded that a second modification of P_2S_5 exists, probably of lower molecular weight than the ordinary variety. The authors have now confirmed this assumption, and find that of the two modifications the new variety is more soluble in carbon disulphide than the ordinary modification. They have investigated the molecular weight of the ordinary sulphide, by determining the raising of the boiling-point in carbon disulphide solution, and have found that the formula in boiling CS_2 is P_4S_{10} . Similar experiments with the new variety show that it contains a substance which has a smaller molecular weight than P_4S_{10} , but on the basis of the molecular weight determinations, and also from the fact that the new variety does not possess a sharp melting-point, it seems probable that it is not a single substance, but that it cannot be further decomposed by fractional crystallisation from carbon disulphide. The following table compares the two modifications:—

	Ordinary pentasulphide.	New variety.
Preparation.	Repeated crystallisation of the raw sulphide from hot CS_2 .	Rapid condensation of vapours of ordinary sulphide, washing with CS_2 , and crystallising the solution.
Appearance	Light yellow crystals, fairly stable in air.	White crystals, giving off H_2S in the air.
Solubility in boiling CS_2	1 : 195.	1 : 30.
Density ..	2.03.	2.08.
M. p. . .	275° — 275° .	Greater part melts at 255° ; entirely fused at 275° .
Mol. wt. in boiling CS_2	444, i.e., P_4S_{10} .	Abt. 360, i.e., between P_2S_5 and P_4S_{10} .

MEETINGS FOR THE WEEK.

WEDNESDAY, 25th.—Society of Dyers and Colourists, 8. "The Dyeing of Wool Mats," by J. W. Lamb.

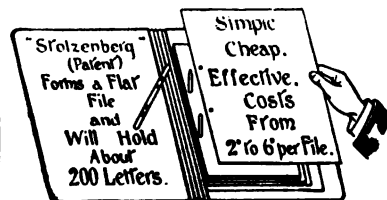
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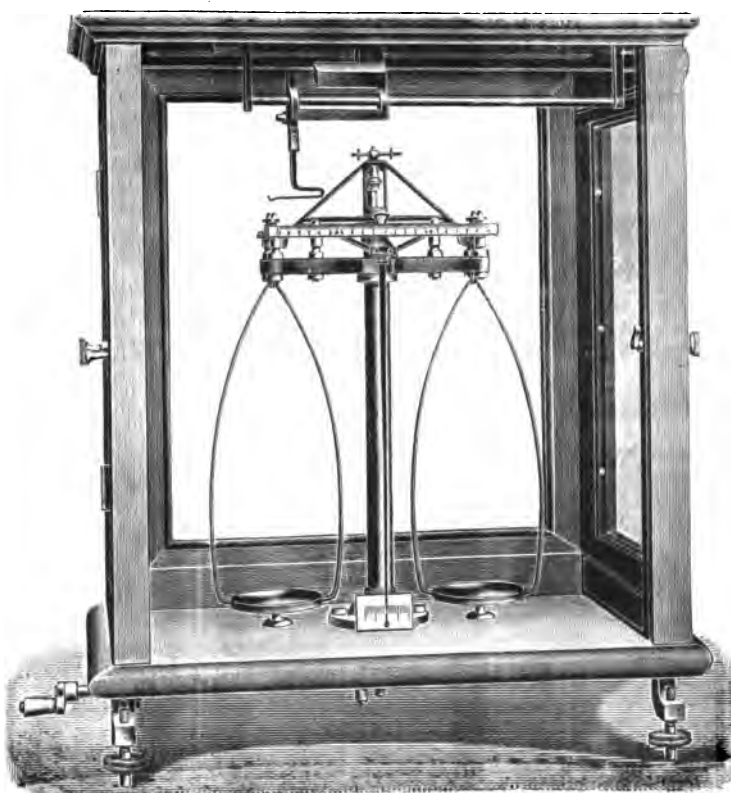
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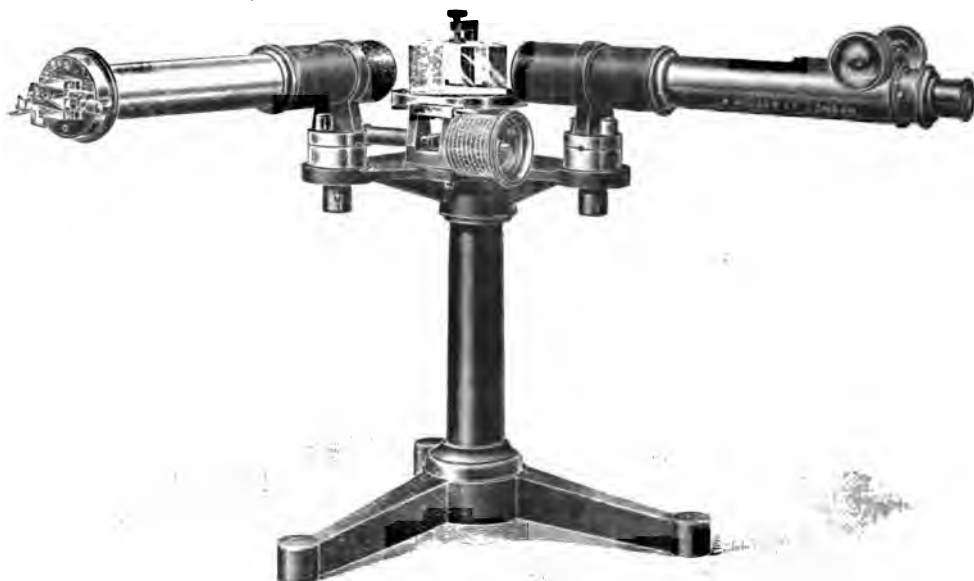
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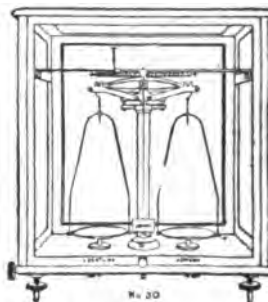
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STUDIES WITH THE LIQUID HYDROGEN AND AIR CALORIMETERS.*

By Sir JAMES DEWAR, M.A., LL.D., Sc.D., F.R.S., Professor of Chemistry at the Royal Institution, and Jacksonian Professor, University of Cambridge.

(Concluded from p. 184).

II. Latent Heats.

In the course of my experiments on the specific heat of diamond, graphite, and ice by means of the liquid hydrogen and air calorimeters, the frequent determination of the quantities of gas evaporated by lead in the same circumstances as the diamond, graphite, or ice under investigation afforded means for the direct measurement of the latent heats of hydrogen, nitrogen, oxygen, and air at their respective boiling-points. The same data for lead† were adopted as were used on the former occasion. The volumes of gas evaporated had, however, to be reduced to 0° C. and 760 m.m. of pressure. If C be the number of cubic centimetres of gas evolved per grm. of lead, measured at 0° C. and 760 m.m., while the lead cools from t° to t° ,

m the number of grms. mass of gas per c.c. under standard conditions, and s' the mean specific heat of lead between t° and t° , then L , the latent heat of the gas, is given by—

$$L = \frac{t' - t}{m C} s'.$$

Table VII. contains a summary of the results obtained. The details of three sets of observations show how closely the results are in accord. (See Table VIII.).

The latent heat of hydrogen, determined from these nineteen observations—some through the short fall of temperature from liquid air, some through the much larger fall from ordinary temperatures—may be taken as very closely 123 grm.-calories. Considering the great mobility of liquid hydrogen, and its small density, it might be imagined that some spray would get carried up by the hollow enclosing gas bubbles. If this took place in the experiments, then the latent heat would be too small. In like manner any solid air carried down from the neck of the calorimeter would have an effect of the same kind. If, however, the transit of the lead into the liquid hydrogen was impeded by a solid air constriction in the neck, or above, then the latent heat would be increased.

In my Bakerian Lecture, the latent heat of hydrogen was taken to be about 200 units, from which I made the following deduction (*Proc. Roy. Soc.*, June, 1901, lxviii., p. 361):—"The order of the specific heat of liquid hydrogen has been determined by observing the percentage of liquid that has to be quickly evaporated under exhaustion in order to reduce the temperature to the melting-point of hydrogen, the vacuum vessel in which the experiment is made being immersed in liquid air. It was found that in the case of hydrogen the amount that had to be evaporated was 15 per cent. This value, along with the latent heat of evaporation, gives an average specific heat of the liquid between freezing- and boiling-point of about 6." The

* A Paper read before the Royal Society, June 8, 1903.

† Behn (*Ann. d. Physik.*, 1900, [4], i., p. 261) gives specific heat of lead as 0.0300 from 18° to -79°, and 0.0291 from -79° to -186°, whence we get 0.0295 from 18° to -186°. From 100° to 18° he gives the value 0.0310, but adds that this is the "mean of known results." Later Schmitz (*Proc. Roy. Soc.*, 1903, lxvii., p. 192) gives the specific heat of lead as 0.0293 at -85°, and 0.0305 at +60°.

TABLE VII.

Substance.	No. of expts.	Fall of temperature.	Latent heat.	Mean.
Oxygen	6	17° to -182.5°	51.72	51.15
	3	16.4 -182.5	51.08	
	5	-78 -182.5	50.65	
Nitrogen	3	18.4 -195.5	50.4	50.4
	4	17 -195.5	48.1	
	4	-78 -195.5	52.7	
Hydrogen	5	17 -252.5	122.9	123.1
	4	17 -252.5	123.6	
	4	-188 -252.5	124.3	
	6	-188 -252.5	121.5	

TABLE VIII.

Weight of lead.	Volume of gas.	Gas per grm. of lead.	Mean.	Reduced to 0° C. and 760 m.m.	Latent heat.
Grm.	C.c.	C.c.			
<i>Oxygen</i> .—From -78° to -182.5°; Barometer, 760.9 m.m.; Temperature, 16.4°.					
1.529	67	43.83	44.30	41.84	$LO = \frac{104.5^{\circ} \times 0.0290}{0.00143 \times 41.84} = 50.65$
1.503	67	44.58			
1.545	68	44.01			
1.431	64	44.73			
1.567	69.5	44.35			
<i>Nitrogen</i> .—From 18.4° to -195.5°; Barometer, 760 m.m.; Temperature, 18.4°.					
0.471	50	106.2	106.3	99.59	$LN = \frac{213.9^{\circ} \times 0.0295}{0.001257 \times 99.59} = 50.41$
0.641	68	106.1			
0.657	70	106.5			
<i>Hydrogen</i> .—From 16.4° to -252.5°; Barometer, 753 m.m.; Temperature, 16.4°.					
0.160	117	731.2	760.5	710.8	$LH = \frac{268.9^{\circ} \times 0.0291 \times 1000}{0.0896 \times 710.8} =$
0.147	116	789.0			
0.122	94	770.5			
0.147	112	761.9			
0.104	78	750.0			

result of the present investigation enables me to correct this statement, the specific heat of the liquid between the boiling- and the freezing-point being 3.4 instead of 6. It appears, therefore, that hydrogen, instead of following the law of Dulong and Petit, has an atomic heat of only half the required amount. In my paper on "The Physical Constants of Hydrogenium (*Trans. Roy. Soc. Edin.*, 1873), it was shown that the specific heat of hydrogen absorbed in palladium was at least 3.5. It seems therefore that hydrogen in the gaseous, the occluded, and the liquid condition has substantially the same specific heat.

In the Bakerian Lecture (*loc. cit.*), I noted for comparison with the specific heat of liquid hydrogen that when liquid nitrogen was similarly treated, "the resulting specific heat of the liquid came out 0.43, or about 6 per atom." Alt, in a recent direct determination of this quantity, gives the value 0.430 (*Ann. d. Physik.*, April, 1904, [4], xiii., p. 1027). This corroboration of the old determination of the specific heat of liquid nitrogen by the evaporation method, adds confirmation to the value now found for the similar constant for hydrogen.

Further corroboration of this value of the latent heat of hydrogen is afforded by Clapeyron's equation,—

$$\text{Latent heat} = (v - u) t \frac{dp}{dt};$$

where v and u are the specific volumes of the gas and the liquid at temperature (absolute) t and pressure p . With this equation we must combine either a Rankine or a Willard Gibbs relation between vapour pressure and temperature. From some early observations with the helium thermometer on the vapour pressure of hydrogen below its boiling-point, I found the Rankine equation—

$$\log p = 5.5038 - \frac{53.13}{t}.$$

Hence, noting that the density of liquid hydrogen at the boiling-point is 0.07, and the specific volume of the gas at the same temperature is 818.7 c.c., Clapeyron's equation gives 120.3 as the latent heat of liquid hydrogen.

A corresponding mean Rankine formula, based on Travers' smoothed results (*Phil. Trans.*, 1902, A, cc., p. 169), gave the latent heat as 119. On the other hand, two Willard Gibbs' equations, calculated from actual observations as evenly distributed as possible, gave the results 123.4 and 117.5, or a mean of 120.5. Thus, while theoretical results seem somewhat lower than those of observation, both point to a value of the latent heat of hydrogen about 121 or 122 gm.-calories.

In the case of nitrogen the observations seem equally good, and we get its latent heat about 50.4 gm.-calories. Determinations of this quantity by former observers are in very fair accord with this value. A careful investigation by Fischer and Alt gave 48.9 (*Ann. d. Physik.*, 1902, [4], ix., p. 1180), and more recently Alt (*Ibid.*, 1904, [4], xiii., p. 1024) gives 48.7 at 718 m.m. pressure (-196.2°) and 52.07 at 96 m.m. pressure (-210.05°). Again, Shearer found in two series of experiments the slightly higher value 49.8, a result (he says) which "agrees very well with that computed from the vapour tension which gives 49.25" (*Phys. Rev.*, 1903, xvii., pp. 124, 471).

From observations of my own on the vapour density of nitrogen between the boiling- and melting-points, I deduced a Rankine formula,—

$$\log p = 6.6462 - \frac{292}{t},$$

which leads to 48.03 for the latent heat of the liquid. In similar circumstances from Fischer and Alt's results, I find the value to be 49.65, while a Willard Gibbs formula from the same observations gives 51.4. The ratio of the liquid to the gaseous volume at the boiling-point being only 1/177, the correction on this account may be neglected in using Clapeyron's equation.

The value of the latent heat of oxygen is found to be 51.15 gm.-calories, the result of fourteen observations, with a possible divergence of half a calorie each way.

Among the most recent determinations of the latent heat of oxygen, Shearer gives the results of two series of observations as 60.9 and 61.0, and adds 60.8 as the result of "thermodynamic computation" (*Phys. Rev.*, 1903, xvii., pp. 124, 469–475). Estreicher, by an electric method, finds this quantity to be 58 calories per gm. (*Acad. Sci. Crac.*, 1904, *Bull.* 3, pp. 183–186; *Science Abstracts*, "Physics," June, 1904, No. 1441). These results are so high compared with other determinations that they must be received with some caution. A direct and careful series of observations by Alt (*Ann. d. Physik.*, 1904, [4], xiii., p. 1020), also by an electric method, gives 52.07 as the latent heat of oxygen at -182.8° (pressure 725 m.m.), rising to 58.85 at -201.3° (pressure 68 m.m.).

Olzewski, Estreicher, and Travers have made observations on the vapour density of oxygen which enable us to calculate its latent heat. Three Willard Gibbs' equations were calculated from Olzewski's observations between the critical-point and the boiling-point, from which a mean value of 51.4 was found (*Comptes Rendus*, 1885, vol. c., p. 351; *Nature*, 1895, vol. li., p. 355; *Phil. Mag.*, 1895, vol. xl., p. 210). A careful examination and selection from Estreicher's three sets of observations between the boiling- and the melting-point led to a Willard Gibbs' equation from which the latent heat was found to be 52.53 (*Phil. Mag.*, 1895, vol. xl., pp. 458, 459). From Travers' smoothed results a series of six Rankine formulae was calculated between 90.7° and 79.17° (absolute), from which the mean value of the latent heat was found to be 53.78 (*Phil. Trans.*, 1902, A, vol. cc., p. 152). The ratio of the liquid to the gaseous volume of oxygen at its boiling-point being only 1/255, its effect in the Clapeyron equation may be neglected.

As between oxygen and nitrogen it would appear that the former has the greater latent heat, a result to be expected if we rely on the constancy of Trouton's constant, namely, that the molecular latent heat is proportional to the absolute temperature of the boiling-point. We may determine the ratio of these two latent heats independently of the value of the specific heat of lead, by selecting observations over approximately the same range of temperature, for we have noted how slight is the variation of the specific heat of lead per degree of temperature. On examining the details of the possible sets of observations that may be compared, I select the set for nitrogen in which a mean of 106.3 c.c. of gas per gm. were given off. This, reduced to 0° and 760 m.m., became 99.59 c.c., over a range of temperature from 18.4° to -195.5° . Two sets of oxygen observations seem equally good, namely, the first two. In the former of these the mean volume of gas given off per gm., reduced to 0° and 760 m.m., was 79.38 c.c., over a range of temperature from 17° to -182.5° ; and in the latter 80.34 c.c. were given off in the same standard circumstances over a range from 16.4° to -182.5° .

Combining these last two with their relative weights of 6 and 3, we get, putting s' for the specific heat of lead, and w for the weight of 1 c.c. of hydrogen,—

$$LO = \frac{198.9^\circ + 2 \times 199.5^\circ}{(80.34 + 2 \times 79.38) \times 16w} s',$$

while from the nitrogen observations we have—

$$LN = \frac{213.9^\circ}{99.59 \times 14w} s',$$

Hence—

$$\frac{LO}{LN} = \frac{597.9^\circ \times 99.59 \times 14}{213.9^\circ \times 239.10 \times 16} = 1.09.$$

This result confirms us in the view that the latent heat of oxygen is greater than that of nitrogen.

Similar ratios between the latent heats of hydrogen and oxygen and hydrogen and nitrogen are of importance in themselves, having regard to future work, and even although the ranges of temperature may not be coincident,

nevertheless the change in the value of the specific heat of lead will not affect the ratios by much more than about 1 per cent, supposing we take the specific heat of lead to be the same in both.

Thus, taking two of the longest ranges for temperature, namely, hydrogen from 17° to -252.5° and oxygen from 17° to -182.5° , we get the ratio—

$$\frac{LH}{LO} = \frac{16 \times 79.58 \times 269.0^{\circ} \times 0.0291}{1 \times 710.78 \times 199.5^{\circ} \times 0.0295} = 2.38;$$

similarly, taking two short ranges, namely, hydrogen from liquid air and nitrogen from solid carbonic acid, we find—

$$\frac{LH}{LN} = \frac{14 \times 51.46 \times 64.5^{\circ} \times 0.0280}{1 \times 162.22 \times 117.5^{\circ} \times 0.0290} = 2.35.$$

From the former of these with $LO = 51.15$, we get $LH = 121.7$; and from the latter with $LN = 50.4$, we get $LH = 118.4$.

The latent heat of air is a quantity whose determination is of a different order from that of either oxygen or nitrogen, seeing that the liquid evaporated is not always of the same composition, and the composition has not always been noted. Behn made a determination of it, and found its value to be 50.8 grm.-calories (*Ann. d. Physik.*, 1900, IV., i., p. 271). But in dealing with this value later in his paper, he takes the composition of the liquid air employed as containing 93 per cent of oxygen. This result may therefore be more appropriately used as a lower limit to the latent heat of oxygen, and thus far as a corroboration of the present value found for oxygen. D'Arsonval states, without giving any details, that he found the latent heat of air to be 65 calories (*Comptes Rendus*, 1901, vol. cxxxiii., p. 983). Shearer has examined this quantity carefully on two occasions, using the same method each time (*Phys. Rev.*, 1902, vol. xv., p. 191; 1903, vol. xvii., p. 472). He distinguishes clearly the effects of various compositions. In his earlier experiments he found that for air containing from 21.8 to 72 per cent of oxygen, the latent heat varied from 44.02 to 51.7 grm.-calories. In his later series, he found that for air containing from 48 to 90 per cent of oxygen, the latent heat rose from 50.6 to 59 grm.-calories. Still more recently Fenner and Richtmyer (*Phys. Rev.*, 1905, vol. xx., p. 81), employing Shearer's method, find that from about the composition of atmospheric air until the mixture contains about 94 per cent of oxygen (from their diagram) the latent heat remains apparently constant at 50.966 , and that then it appears to rise rapidly to 54.10 at 97.6 per cent of oxygen. They seem to accept 61 grm.-calories as the latent heat of oxygen, so that the increase from 97.6 per cent to 100 per cent is exceptionally rapid.

In the present series of observations, the liquid air employed was old, that is, it was very rich in oxygen. If therefore we take the density of the air in the gas-receiver as being equal to that of oxygen, we shall have values of the latent heat of liquid air erring by defect. In the earliest experiment the volume of gas given off was (at 0° , and 760 m.m.) 84.25 c.c. per grm. of lead, from 18.5° to -184.5° , whence—

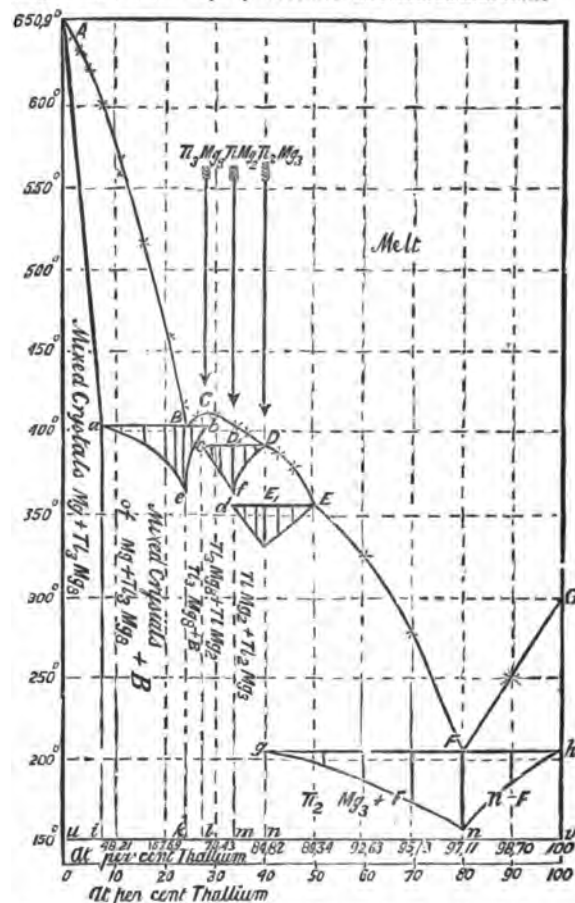
$$L_{air} = \frac{0.0295 \times 203^{\circ} \times 1000}{84.25 \times 1.43} = 49.7.$$

Similarly in a later case from 17.9° to -188° , the volume per grm. of lead was (at 0° and 760 m.m.) 79.54 c.c., whence $L_{air} = 53.41$. After this, several series of experiments were made in which a succession of half grms. of lead, 10 or 12 at a time, were dropped into old liquid air. In one experiment where 12 half grms. were employed, the mean volume of gas given off per grm. was (at 0° and 760 m.m.) 76.52 c.c., and the range of temperature was from 10.9° to -188° , thus giving the latent heat of air as 53.63 . These last values come very near those found by Fenner and Richtmyer; but the results are so varied that it is clear the question of the latent heat of air of very high oxygen concentration is one requiring further investigation.

MAGNESIUM-THALLIUM ALLOYS.

By GEORG GRUBE.

AN accurate investigation of the alloys of magnesium and thallium has not yet been performed. Carstanjen (*Zeits. Prakt. Chem.*, 1867, cii., 84), for purely practical purposes, prepared an alloy with 50 per cent thallium and 50 per cent magnesium, in the hope of thus obtaining a material which would burn with an intensely green light, and would perhaps find technical application. It was found, however, that this alloy burnt with the colour of ordinary magnesium wire. As regards the properties of the alloy with 50 per cent thallium, he states that it is far less stable in air than pure magnesium, that it rapidly becomes discoloured and turns



grey, and, then covered with moist caustic thallous oxide. Mellor (*CHEMICAL NEWS*, 1867, xv., 245) prepared alloys with 5, 10, 15, 25, and 50 per cent thallium, and makes the following statement concerning their properties:—"An alloy with 5 per cent thallium seems to make the magnesium less brittle and more ductile, but the alloys richer in thallium, e.g., those with 25 and 50 per cent thallium, are much more easily oxidised than pure magnesium."

Thus no information is to be found concerning the solidification points of the magnesium-thallium alloys, nor regarding the question whether in the series of the alloys chemical compounds of magnesium and thallium exist. The aim of this research is to examine the properties of the magnesium-thallium alloys on the basis of the method of thermal analysis.

The experimental arrangement of my earlier work was found suitable for determining the cooling curves. The

TABLE I.

Proportion of Tl in alloys.		Temperature of the breaks.	Eutectic crystallisation.							
Weight, per cent.	Atoms, per cent.		Temp.	Time.	Temp.	Time.	Temp.	Time.	Temp.	Time.
0	0		Melting-point of pure Mg, 650°9'; time of crystallisation, 125 secs.							
10.00	1.04	639.4°	—	—	—	—	—	—	—	—
20.00	2.90	632.1	—	—	—	—	—	—	—	—
30.00	4.87	623.7	—	—	—	—	—	—	—	—
40.00	7.38	600.2	—	—	—	—	—	—	—	—
50.00	10.66	577.6	402.4	23	—	—	—	—	—	—
60.00	15.18	519.3	401.0	37	—	—	—	—	—	—
70.00	21.78	477.1	404.2	85	—	—	—	—	—	—
72.50	23.94	417.1	405.9	120	—	—	—	—	—	—
73.64	25.00	408.8	405.7	55	—	—	—	—	—	—
75.00	26.37	411.3	403.2	15	—	—	—	—	—	—
76.06	27.50	Separation of Tl_3Mg_8 at 412.9°; time of crystallisation, 145 secs.								—
77.50	29.13	412.3	—	—	393.2	25	—	—	—	—
78.78	30.70	411.2	—	—	393.0	60	—	—	—	—
80.73	33.33	405.0	—	—	392.9	100	—	—	—	—
82.50	36.00	399.5	—	—	392.4	30	355.2	35	—	—
83.70	38.00	395.9	—	—	392.9	20	355.6	60	—	—
84.82	40.00	389.8	—	—	—	—	355.5	85	—	—
86.10	42.50	386.0	—	—	—	—	355.4	60	—	—
87.50	45.52	377.8	—	—	—	—	355.4	40	205.2	10
90.00	51.79	353.7	—	—	—	—	—	—	204.6	25
92.63	60.00	325.3	—	—	—	—	—	—	205.2	60
95.00	69.40	278.4	—	—	—	—	—	—	205.6	105
97.11	80.00	—	—	—	—	—	—	—	205.2	155
98.70	90.00	251.3	—	—	—	—	—	—	205.3	65
100.00	100.00	Melting-point of pure Tl, 301.6°; time of crystallisation, 160 secs.								—

breaks and critical-points of the curves were clearly shown. The oxidation of the alloys prepared in a current of hydrogen was exceedingly slight. By performing a few analyses it could be shown that the concentration of the alloys had not been appreciably displaced by burning. The thermo-element used to measure the temperature and the galvanometer were tested for constancy at the beginning and end of the investigation, by determining the melting-points of antimony, zinc, and lead. The temperature results of the cooling curves calculated on the scale of the air thermometer, as well as the times of crystallisation determined from them, are collected in Table I.

The table gives in the first column the proportion of thallium in the alloys in atoms and weight per cent. The second column gives the temperatures of the breaks; these are the temperatures at which the separation of a crystalline form begins. In the third column are the temperatures of the eutectics and their times of crystallisation in seconds. The temperatures can in all cases be determined correct to $\pm 1^\circ$, and the times of crystallisation to within ± 5 seconds. The concentrations of the alloys were weighed correct to 0.01 grm.

On the basis of the temperatures and times of crystallisation collected in Table I., the diagram of the magnesium-thallium alloys given in the figure was drawn. The concentrations, corresponding to the abscissæ, are expressed in atoms per cent, because then the diagram is clearer. The temperatures are represented by the ordinates.

The curve A, B, C, D, E, F, G represents the fusion-curve of the magnesium-thallium alloys; i.e., it connects with one another all the points at which the crystallisation of the crystalline form primarily separating begins. The eutectic horizontals are drawn through the points B, D, E, and F, and by dropping the perpendiculars proportional to the times in the usual way the eutectic curves are constructed.

The fusion-curve sinks from the melting-point of pure magnesium A in a curved line to the eutectic point B. The point B occurs at a concentration of 24 atoms per cent thallium and at a temperature of 403.7°.* From the point B the fusion-curve rises to the point C, from which it falls to the point D, at which the concentration amounts to 40 atoms per cent thallium. At C the fusion-curve has a

true maximum. Through the point D also a eutectic horizontal passes, the temperature amounting to 392.9°. From D the fusion-curve sinks further to E, through which the eutectic horizontal $d\epsilon$ passes, which occurs at a temperature of 355.4°. The point E occurs at a concentration of 50 atoms per cent thallium. At E there is again a break in the curve. The curve then falls from E to its lowest point, F. From the point F the curve rises in a straight line to the melting-point of thallium, G. The point F occurs at a concentration of 80 atoms per cent thallium, at a temperature of 205.2°.

The examination of the fusion-curve shows us that a true maximum occurs on it at the point C, and two hidden maxima in the parts of the curve CD and DE. This shows the existence of three chemical compounds of magnesium and thallium.

In order to determine the formulæ of these compounds we applied the methods we have already described (*Zell. Anorg. Chem.*, xlv., 123). Applying these methods first to the maximum C:—

1. The duration of the eutectic crystallisation at 403.7° becomes equal to zero at the point b, at 27.6 atoms per cent thallium, if we follow the course of the curve ϵb ; the duration of the eutectic crystallisation at 392.9° becomes zero at 27.3 atoms per cent thallium, as shown by the course of the curve ϵf . The mean of these two values is 27.45 atoms per cent thallium.

2. By graphic interpolation from the observed points of the fusion-curve, the maximum was found at about 27.4 atoms per cent thallium.

3. The alloy with 27.50 atoms per cent thallium has the cooling curve of a pure substance, with a time of crystallisation of 145 seconds. The critical-point lies higher than the temperature of the beginning of crystallisation in the neighbouring alloys.

The formulæ to be considered for the compound at the maximum C are Tl_2Mg_5 with 26.37, Tl_3Mg_7 with 30.00, and Tl_3Mg_8 with 27.26 atoms per cent thallium. The mean value established by the above three methods for the concentration of the compound amounts to 27.45 atoms per cent thallium. The formula Tl_3Mg_8 is closest to this value. In order to determine whether the concentration of the maximum had been somewhat displaced by burning, three alloys from the concentration region in question were analysed, the magnesium being weighed as pyrophosphate

* For the eutectic temperatures in the diagram the mean values are taken from the eutectic temperatures given in Table I.

and the thallium as thallous iodide. Each analysis was repeated. The results are given in Table II.

TABLE II.

Weighed composition in atoms per cent.		Determined by analysis. Atoms per cent.	
Tl.	Mg.	Tl.	Mg.
26.37	73.63	1. 26.46	73.49
		2. 26.55	73.65
27.50	72.50	1. 27.56	72.39
		2. 27.59	72.46
29.13	70.87	1. 29.20	70.74
		2. 29.11	70.90

The values found analytically agree to within 0.1 per cent with the concentration of the maximum calculated from the weighed quantities; hence the concentration of the maximum of the fusion-curve is proved to be 27.35 atoms per cent thallium with a possible error of ± 0.1 per cent. We are thus forced to accept the formula Tl_2Mg_3 for the compound crystallising out at the maximum c.

To determine the formulæ of the compounds formed at the eutectic temperatures d and e, we proceed as follows:—

1. The duration of crystallisation at the temperature of the straight line *cd* has a maximum at the point *d*, at a concentration of 33.33 atoms per cent thallium.

2. The duration of crystallisation on the straight line *ed* becomes zero at the point *d*, with a percentage of thallium = 33.4 atoms per cent.

The concentration of 33.33 atoms per cent thallium corresponds to the formula $TlMg_2$. The agreement of the values given under 1 and 2 for the composition of the compound proves the correctness of the formula $TlMg_2$.

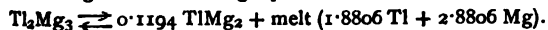
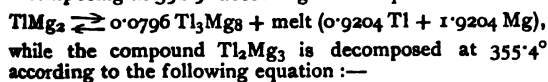
In the same way we determine the composition of the compound formed at the temperature of the horizontal *e*:—

1. The duration of crystallisation at the temperature of the straight line *de* has its greatest value at a concentration of 40.00 atoms per cent thallium.

2. The duration of eutectic crystallisation at the temperature of the straight line *gh* becomes equal to zero at the point *g*, at a concentration of 40.2 atoms per cent thallium.

The formula Tl_2Mg_3 corresponds to a concentration of 40 atoms per cent thallium, and we must therefore accept it for the compound crystallising at the point *e*.

The compound Tl_3Mg_8 melts to a homogeneous liquid, because a maximum occurs on the fusion-curve at the composition of this compound. The two other compounds, $TlMg_2$ and Tl_2Mg_3 , when they melt, split up into crystals of different composition and melts, the compound $TlMg_2$ decomposing at 392.9° according to the equation—



It now remains to be decided whether pure magnesium crystallises from the melt which is poor in thallium, and pure thallium from the melt which is rich in thallium. The duration of crystallisation at the temperature of the eutectic horizontal, *h g*, becomes equal to zero at the concentration of pure thallium. There is therefore no reason for assuming the existence of mixed crystals in the concentration region below the line *f g*. This question was not investigated further microscopically, because such an examination is rendered very difficult owing to the great variability of, and the difficulty of polishing, the soft conglomerate. The duration of eutectic crystallisation at a temperature of 403.7° becomes equal to zero at 7 atoms per cent thallium, as may be seen from the diagram. We are therefore compelled to assume that from the melts rich in magnesium, pure magnesium does not crystallise out, but a series of mixed crystals, the last member of which contains 7 per cent thallium. The concentration of the saturated

mixed crystals of this series may be determined by extrapolation of the eutectic times on the straight line *a b*.

The microscopic examination of the polished surfaces of alloys between 0 and 7 atoms per cent thallium must thus reveal a perfectly homogeneous structure; it is supposed that the rate of cooling of the alloys is so slow that the exchange between melt and primarily separated crystals can take place completely. The examination of the polished surfaces gave the following results:—Those of alloys with 1.04 and 2.90 atoms per cent thallium had a perfectly homogeneous structure. A specimen with 4.87 atoms per cent thallium, however, still contained some eutectic, *B*. But by keeping the temperature of this alloy for about half-an-hour between 440° and 405°, the eutectic might be almost completely removed.

The following remarks may be made concerning the fields of the diagram:—Above the curve *A, B, C, D, E, F, G* all alloys are liquid. In the fields bounded by the fusion-curve and the eutectic horizontal there is always a crystalline form in equilibrium with melt. Below the eutectic horizontals, thus below the line *A a*, the alloys are perfectly solidified. The fields are compared in Table III.

TABLE III.—Fields.

I. Liquid Region:—Limited on the lower side by the fusion-curve *A, B, C, D, E, F, G*.

II. Region with one crystalline form:—

<i>A a i a</i> ..	Mixed crystals of $Mg + Tl_3Mg_8$.
<i>A B a</i> ..	Mg.
<i>C B b</i> ..	Tl_3Mg_8
<i>C D c</i> ..	Tl_3Mg_8
<i>D i D E d</i> ..	$TlMg_2$
<i>E i E F g</i> ..	Tl_2Mg_3
<i>F G h</i> ..	Tl

III. Region with two crystalline forms:—

<i>a b k i</i> ..	Mixed crystals of $Mg + Tl_3Mg_8$ + eutectic [$Mg + Tl_3Mg_8$].
<i>B b l k</i> ..	Tl_3Mg_8 + eutectic [$Mg + Tl_3Mg_8$].
<i>c D i m l</i> ..	Tl_3Mg_8 + $TlMg_2$.
<i>d E i w m</i> ..	$TlMg_2$ + Tl_2Mg_3 .
<i>g F n w</i> ..	Tl_2Mg_3 + eutectic [$Tl + Tl_2Mg_3$].
<i>F h v n</i> ..	Tl + eutectic [$Tl + Tl_2Mg_3$].

A microscopic examination of the alloys was then performed in order to prove the results obtained from the fusion diagram. The polished specimens with 0 to 7 atoms per cent thallium have already been described. The alloys between 7 and 24 atoms per cent thallium must consist of saturated mixed crystals with 7 atoms per cent thallium, surrounded by eutectic *B*. The eutectic *B* is composed of small saturated mixed crystals and small crystals of the compound Tl_3Mg_8 . The photograph, magnified sixty times, of a polished surface with 15.18 atoms per cent thallium, etched by standing in the air, shows primarily formed branching white mixed crystals, surrounded by blackened eutectic *B*, the constituents of which cannot be recognised, because they blacken instantly in the air. Between 24.00 and 27.26 atoms per cent thallium, primarily separated crystals of the compound Tl_3Mg_8 must exist, surrounded by eutectic *B*. The photograph, magnified fifty times, of a polished surface with 26.37 atoms per cent thallium, etched by allowing to stand in air for a short time, shows clearly the blackened primarily separated crystals of the compound Tl_3Mg_8 surrounded by eutectic *B*. As the surface was exposed to the air only for a very short time, the constituents of the eutectic can still be recognised.

The alloys between 27.26 and 33.33 atoms per cent thallium should, according to the diagram, contain the compounds Tl_3Mg_8 and $TlMg_2$. The photograph of a polished surface with 29.13 atoms per cent thallium shows white crystals of the compound $TlMg_2$ surrounded by the compound Tl_3Mg_8 . As we are now in the immediate neighbourhood of the maximum *c*, the quantity of the compound Tl_3Mg_8 is very large, and the secondarily formed

crystals of TlMg_2 are therefore embedded in the compound Tl_2Mg_3 .

The alloys between 33.33 and 40.00 atoms per cent thallium consist of primarily formed compound TlMg_2 and secondarily separated compound Tl_2Mg_3 . The photograph of a polished surface with 36.00 atoms per cent thallium, which is etched by standing a long time in air, shows the primarily separated clear crystals of the compound TlMg_2 arranged in lines; they are surrounded by the compound Tl_2Mg_3 , which very rapidly blackens in air owing to oxidation.

It is very difficult to photograph the polished surfaces of alloys which contain the primarily formed compound Tl_2Mg_3 because of the extraordinarily rapid oxidation of the compound in air. When freshly prepared it consists of fairly long silvery white crystalline needles, which, however, are exceedingly unstable in air. Photographs of a polished surface with 45.52 atoms per cent thallium show these white needles of the compound Tl_2Mg_3 strongly attacked by oxidation, surrounded by a black mass, which consists partly of oxidised compound and partly of the eutectic F .

As has been repeatedly mentioned before, the thallium-magnesium alloys are blackened by oxidation in the air. In damp air they are attacked more rapidly than in dry air. Of the three thallium-magnesium compounds, Tl_2Mg_3 is oxidised most quickly and Tl_2Mg_2 rather more slowly, while TlMg_2 is the most stable. The difference of the stability of the three compounds is, however, not great.

In conclusion I wish to express my hearty thanks to Professor Tammann for suggesting this work to me, and for his kind advice and assistance.—*Zeit. Anorg. Chem.*, xlvii., 84.

ALTERNATE CURRENT ELECTROLYSIS.*

By ERNEST WILSON, M.I.E.E.,
Professor of Electrical Engineering, King's College, London.

It is well known that if an alternate current be passed between metal electrodes in an electrolyte, electrolysis may take place. For instance, it has been shown that, in the case of lead plates in dilute H_2SO_4 , the SO_4 combines with the lead to form PbSO_4 , and the plates are eaten away. The present paper gives an account of some experiments made to determine what may be the effect upon certain metals of passing alternating currents between them and certain electrolytes under given conditions. Suppose that an alternating current be passed between electrodes in an electrolyte, and that the curves of potential difference between the electrolyte and one electrode and the curve of current be observed. Let the curve of potential difference be corrected for the fall of potential due to the conductivity of the electrolyte, thereby giving the E.M.F. of electrolysis measurable in volts. Let the current curve be integrated, giving the quantity of electricity measurable in coulombs. We should expect that as the maximum coulombs per half period increased, the E.M.F. of electrolysis would also increase until it had the value given by continuous current, and that with further increase of the maximum coulombs per half period the E.M.F. of electrolysis would have a constant amplitude. If the process were truly reversible, we should expect to find that the E.M.F. of electrolysis and current would have an effective phase displacement of one quarter period in time.

The plates in a given cell were of like metal, and were separated $\frac{1}{4}$ inch (0.317 c.m.), with their opposing faces parallel. They were held in position by wooden blocks and ebonite distance pieces bolts and nuts. The wooden pieces covered the back of each plate, with the view of confining the current to the opposing faces. The area of each of the surfaces exposed in the electrolyte was about 150 sq. c.m., but not all of each plate was submerged. For the purpose of obtaining the potential difference

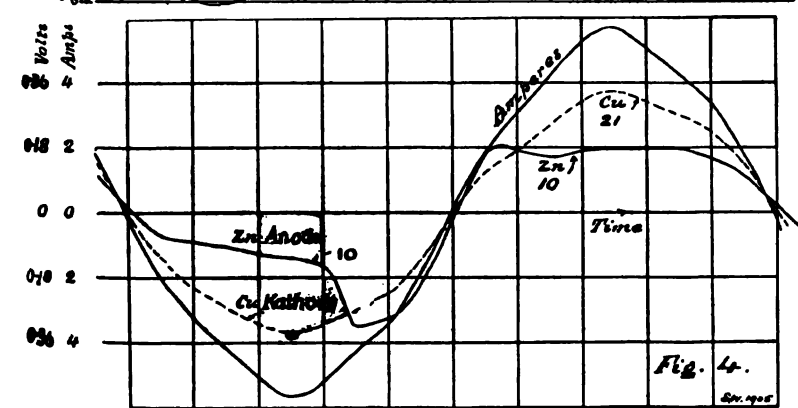
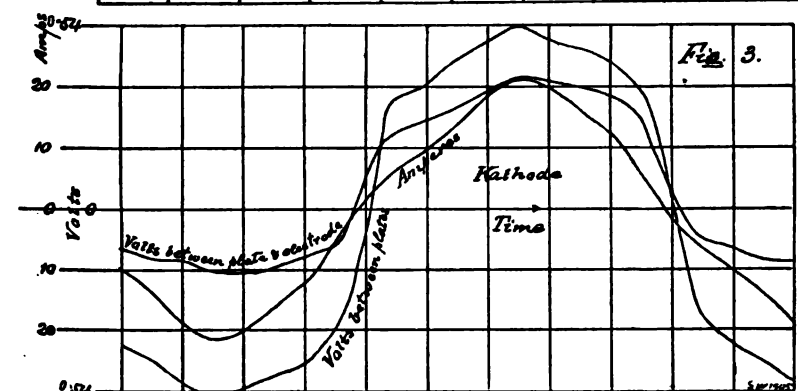
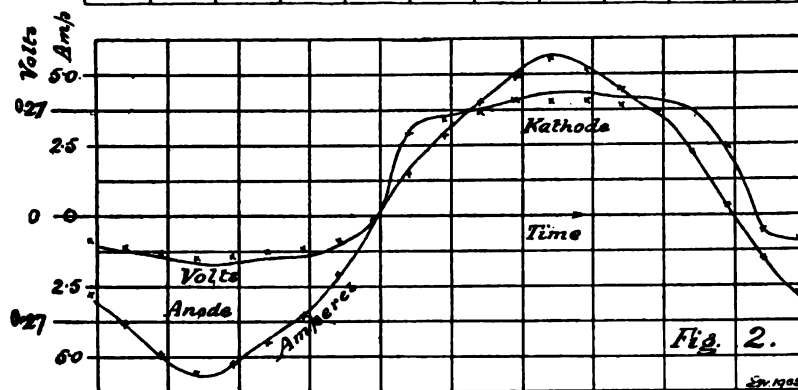
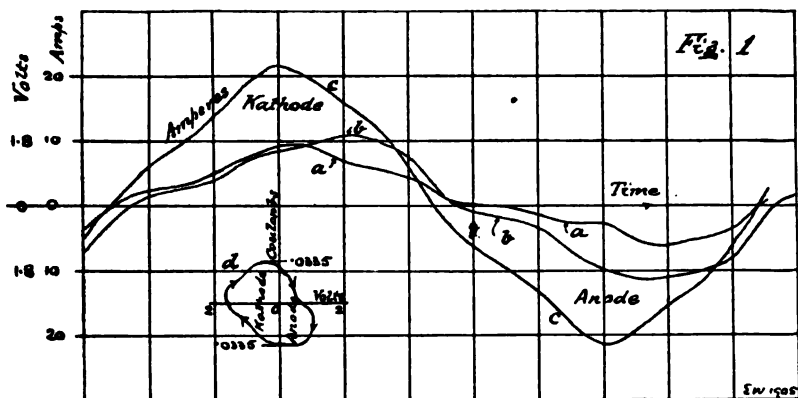
between the electrolyte and one of the plates, an exploring electrode, cut from the plate itself, was placed in the electrolyte midway between the plates, and by the aid of a revolving contact-maker on the alternator shaft and a quadrant electrometer the curve was obtained. The distance between the exploring electrode and the plate was about 1 m.m. Similarly the curve of current was obtained by observing the instantaneous value of the potential difference across a non-inductive resistance placed in the circuit. The curve of current was controlled by inserting a considerable non-inductive resistance in the circuit. The E.M.F. of electrolysis is therefore a dependant variable as regards wave-form. Further research should deal with variation of wave-form. Small test pieces were placed in the solution to see if any action took place without the passage of the electric current. It should be noted that during the experiment the solution in a given cell changes, and therefore an average result has been obtained. No special care was taken to keep the temperature of a given cell constant, and the volume of fluid in each cell was about 2 litres.

Lead.

H_2SO_4 dil.—The electrolysis produced by an alternating current when passed between lead electrodes in dilute H_2SO_4 (100 pts. H_2O + 5 pts. H_2SO_4 by vol.) has already been studied (see *The Electrician*, April 18, 1902). It was shown that for a given R.M.S. current density over the plate, less lead per sq. cm. per hour was dissolved at frequency 92.5 than at frequency 21.5. A R.M.S. density of 0.0236 ampère per sq. c.m. would eat away the lead in one year to a depth of 2.6 c.m. and 4.8 c.m. respectively at the above frequencies. The same current density with direct current would eat away 70 c.m. in a year. Since the R.M.S. current density is the same and the wave-form is the same in the two experiments, the maximum coulombs per half period will vary in the inverse ratio of the frequencies, but we do not find that the dissolved lead varies as the maximum coulombs. Referring to the table, Experiments 1 and 2 show that at frequency 21.5, 0.00629 grm. per hour per sq. c.m. were dissolved. This multiplied by the ratio of the frequencies would give 0.00146 grm. per hour per sq. c.m., as against 0.00344 actually measured. Experiment 3 was undertaken to discover if at 92 frequency and approximately the same maximum coulombs per half period, the weight of dissolved lead would be the same as in Experiment 1. We find that five times as much lead is dissolved at the higher R.M.S. current density. The effect may depend upon the current density, since the maximum coulombs per half period are slightly less in Experiment 3 than in Experiment 1, whereas the current density is nearly four-fold. Also in Experiment 3 the density of the electrolyte fell to 1036 in eight hours, as against 1049 in fifteen hours in Experiment 1.

In Experiment 3, curve *a* Fig. 1 is the potential difference between the lead exploring electrode and one plate. This can also be taken to give the E.M.F. of electrolysis, since the conductivity drop is sufficiently small. The curve *b* is the potential difference between the plates, and *c* is the curve of current. It will be observed that the E.M.F. of electrolysis *a* does not change sign at the moment the plate begins to be an anode; the difference in phase represents the time taken to reverse the E.M.F. existing since the coulombs were last a maximum. The work done during this time is returned to the system. This is not the case when the plate begins to be a kathode, as the reversal of E.M.F. occurs simultaneously with the current. The coulombs have been plotted co-ordinately with the E.M.F. of electrolysis, giving the cyclical curve *d*. As was previously pointed out, more work is done on the system during the time that the plate is a kathode than when it is an anode. The evolved hydrogen combines with the oxygen of the PbO_2 , leading to the formation of PbSO_4 , the maximum coulombs being sufficiently great to produce the peroxide. The plates are not, however, fully polarised in this experiment, much less so in Experiment 2, and it may be that the low result in Experiment 2 is attributable

* A Paper read before the Faraday Society, July 3, 1905.



to the small value of the maximum coulombs. The electrolysis with lead electrodes at low current density is a subject worthy of further research.

It is conceivable that electrolysis by alternating currents may be influenced by diffusion and certain local conditions. When observing the E.M.F. of electrolysis it was noticed that the electrometer deflection became unsteady at certain times of a period, indicating how easily it may be affected. In these experiments the plates were purposely placed near together, and did not give such facilities for diffusion as might otherwise have been obtained.

Zinc.
H₂SO₄ dilute.—The most marked effects with zinc have been obtained when it has been amalgamated and placed in dilute H₂SO₄ (100 pts. H₂O + 5 pts. H₂SO₄ by vol.). In Experiments 4 and 5 the current densities are nearly the same, but the frequencies are different. The dissolved zinc at the higher frequency is greater than we should expect if we simply took the ratio of the maximum coulombs per half period into account. The figures are 0.00147, as against 0.00189 observed, and agree more closely than was the case in Experiments 1 and 2. Again comparing the results of Experiments 4 and 6, in which the maximum coulombs are the same, we find 0.0053 gm. per sq. c.m. per hour dissolved, as against 0.00695 at the higher frequency. It should here be noted that in Experiment 6 the plates were not freshly amalgamated, nor was the solution freshly put up. After weighing at the close of Experiment 5, the plates were again placed in the same solution, and Experiment 6 made. In Experiment 7 freshly amalgamated plates and fresh solution were used, and the result is quite different from that obtained in Experiment 6. To test the importance of the degree of amalgamation and the period of rest between amalgamation and starting the experiment, four new zinc plates were amalgamated to the same degree as nearly as possible, and left nearly three days before being used. Experiments 8 and 9 were then made. Comparing Experiment 9 with 7, in which the duration of test, frequency, and current density were the same, the agreement is better, since the average grms. per sq. c.m. per hour are

respectively 0.00103 and 0.00166. The results no doubt depend upon the preparation of the plates before the experiment.

The full line curves in Fig. 2 were obtained during Experiment 4, and the crosses show the corresponding points obtained during Experiment 5. The agreement as to wave-form, phase, and amplitude of the E.M.F. of electrolysis at the two frequencies demonstrates that in the case of amalgamated zinc in dilute H_2SO_4 a change from 25 to 92 periods per second does not affect the possibility of the E.M.F. of electrolysis taking the same wave-form, amplitude, and phase relation. Experiments made with sufficiently increased frequency might throw some light upon the time taken to accomplish dissociation. Fig. 3 shows the curves obtained during Experiment 7. The phase relations are practically the same, but the effect of conductivity upon the E.M.F. observed between the exploring zinc electrode and one plate when the current is near a maximum, is slightly observable. Test pieces of amalgamated zinc were in the solutions during the experiments, and were practically unchanged in weight.

Zinc Chloride (strong).—The zinc plates in Experiment 10 had, when immersed in the solution, a smooth clean surface, and when taken out after the test they were highly oxidised. In Fig. 4, curve 10 was obtained between the zinc exploring electrode and one plate. The potential difference rises to a maximum of 0.32 volt when the plate is an anode, of which 0.01 volt may be due to conductivity. Curve 10 may be taken to be the E.M.F. of electrolysis, and it is nearly in phase with the current. Although the plates have increased in weight during the experiment, it is due to oxidation which leads to their disintegration.

Zinc Sulphate (saturated).—Experiment 11 has had little or no effect upon the zinc plates immersed in saturated zinc sulphate solution. The potential difference between the zinc exploring electrode and one plate has the same wave-form as, and is in phase with, the current. There is no visible oxidation, and the process is probably almost reversible.

Sodium Sulphate (strong).—Under the conditions of Experiment 12 the zinc plates immersed in this solution have gained in weight, and are still heavier (than before experiment) after being rubbed with wash-leather to remove the surface oxide. The potential difference between the exploring electrode and one plate is shown in Fig. 5, curve 12.

(To be continued).

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY EXAMINATIONS.

To the Editor of the Chemical News.

SIR,—In connection with the subject raised by your correspondent "Technicus" in the CHEMICAL NEWS (vol. xcii., p. 168), I should be very pleased if you would insert the following:—

"Technicus" remarks:—"There are many chemists employed in technological work who have never had the opportunities and advantages which are necessary to become A.I.C. or F.I.C." This raises the question: Why have not the Institute of Chemistry inaugurated examinations for a degree for technical chemists (A.I.T.C. or F.I.T.C.)?

Young chemists employed in iron and steel works, and other laboratories in connection with manufacturing processes, have not the time to study for such examinations as are required to obtain the A.I.C. degree, much less the qualification required—of working under an Associate or Fellow. In order to get the degree, they must proceed in a roundabout way—by qualifying for the B.Sc. degree. This means years of hard work, employing every moment of their spare time, and allowing no time for recreation and fresh air, which those who work in a large ironworks

laboratory will agree is very much a necessity to them. This being the case, why does not the Institute of Chemistry draw up a scheme of examination bringing in those subjects necessary to a technical or metallurgical chemist?

Taking as an example the case of a metallurgical chemist, let me suggest a scheme which would prove useful and suitable for him.

Preliminary Examination.—(a). Elementary Inorganic Chemistry, theoretical and practical. (b). Elementary Iron and Steel Manufacture. (Paper set being similar to City and Guilds examination questions). (c). Practical Metallurgy, elementary. (d). First and Second Stage Mathematics. (e). One of following three subjects:—(1) Elementary Machine Construction and Design, (2) French, (3) German.

Students having already passed Board of Education or City and Guilds of London examinations in any of these subjects, elementary or advanced stages, to be exempted from examination on producing certificates.

Intermediate Examination (no exemption).—(a). Advanced Inorganic Chemistry, theoretical and practical. (b). Elementary Theoretical Organic Chemistry. (c). Advanced Iron and Steel Manufacture. (d). Advanced Practical Metallurgy. (e). Third Stage Mathematics. (f). Two of following three subjects:—(1) Advanced Machine Construction and Design, (2) French, (3) German.

Final Examination.—(a). Analytical Chemistry (this paper to cover the whole of practical work necessary to a first-class chemist, and including questions on the theory of such analysis). (b). Honours Iron and Steel Manufacture. (c). Honours Practical Metallurgy. (d). Fourth Stage Mathematics. (e). French. (f). German.

A scheme of this description would be within reach of any technical chemist with any ambition at all, and would cover the work necessary to him and be at the same time sufficiently difficult to ensure only the really competent ones obtaining the degree. For chemists other than metallurgical, the Iron and Steel and Practical Metallurgy could be replaced by subjects dealing with their special line.

I feel sure that all technical chemists will agree with me that such a scheme as I have here proposed would be beneficial, and ought to be carefully considered by the Institute of Chemistry or some other similar body; and if the Institute have the interests of chemistry at heart, they should not longer delay in such an important matter.

Hoping that this letter may be the means of bringing about the inauguration of some such degree, I am, &c.,

ONE OF MANY.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 14, October 2, 1905.

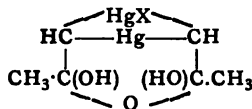
Isostrychnine.—A. Bacovesco and Amé Pictet.—When strychnine is heated with water in sealed tubes to a temperature of 160–180°, it slowly dissolves, and, on cooling, the solution deposits long prismatic needles which fuse at 214.5°. An analysis of this substance shows it to have the formula $C_{21}H_{22}N_2O_4 + 3H_2O$. It is therefore an isomer of strychnine, and is called by the authors *isostrychnine*. Under the action of sodium ethylate this substance is transformed entirely into isostrychnic acid. It can therefore be considered as an anhydride of this acid, in the same way as strychnine is of strychnic acid. The isomerism of the two bases is consequently of the same nature as that of the two acids.

Action of Nitrogen upon Water-vapour.—O. F. Tower.—It has been shown that at high temperatures nitrogen and water-vapour react to a very slight extent according to the equation $N_2 + 2H_2O = 2NO + 2H_2$. The author has now performed experiments to find out whether nitric oxide is formed in measurable quantities, and whether it is accompanied by the equivalent quantities of hydrogen. The nitrogen was generated from ammonium sulphate and potassium nitrite, and purified by passing through sulphuric acid and over ignited copper. The exit gases were tested for nitric oxide by mixing them with oxygen in order to convert the nitric oxide into the dioxide, and the latter was then absorbed in a Winkler's gas burette with 85 per cent sulphuric acid. The acid was shaken up with mercury in a Lunge's nitrometer, and the volume of the nitrogen dioxide read off. In the first experiments, although the temperature amounted to about 2000°, only traces of nitric oxide were found. If sparks were passed through the mixed gases appreciable quantities of nitric oxide were formed. In these experiments the hydrogen set free was determined, and it was found that hydrogen and nitric oxide are formed in equivalent quantities according to the above equation. To obtain equilibrium between nitrogen and water-vapour an electrically heated iridium furnace was used. It was found that the action between nitrogen and water at high temperatures can be increased to any extent by increasing the partial pressure of the nitrogen.

Perchromates.—K. A. Hofman and H. Hiendlmaier. —In preparing ammonium diperchromate from chromium hydroxide or ammonium chromate and hydrogen peroxide in presence of ammonia, the authors find that the amount of ammonia present has a decided influence upon the reaction. If the solution contains either no free ammonia or else ammonia in large excess, crystallised stable products are obtained. It was found that chromic acid mixed with one molecule of hydrogen peroxide in 10 to 20 per cent ammoniacal solution gives no salt, but unites with three ammonia molecules to form the compound $\text{CrO}_4(\text{NH}_3)_3$, which is capable of existing in two forms, the second or β -form being produced when the concentration of the ammonia is the highest possible. Investigation of the perchromate shows that it is not a salt, but an amine. For, according to the results of the elementary analysis and of the oxygen determinations, only 9 hydrogen atoms are present to 3 nitrogen atoms, while 3 ammonium groups would require 12 hydrogen atoms. This of course could be explained by supposing that 2 ammonium groups and 1 amido group are present, but this supposition has been disproved by Wiede. The α - and β -forms behave very similarly, both qualitatively and quantitatively, towards alkalis and acids. To prove that these products are not salts but amines, the action of acetic acid upon them was investigated. It was then found that the three NH_3 molecules of the peroxide $\text{CrO}_4(\text{NH}_3)_3$ are not attacked by strong acetic acid. When it is remembered that both secondary potassium chromate and secondary ammonium chromate give up at least half their alkali with dilute acetic acid, this appears to prove that the peroxide contains no ammonium, but amine groups. If ammonium bichromate solution, ammonium nitrate, and hydrogen peroxide are mixed in the cold, ammonium perchromate, $\text{NH}_4\text{CrO}_5 + \text{H}_2\text{O}_2$, is formed; this has already been prepared by Wiede.

Compounds of Ketones and Aldehydes with Mercury Oxide.—S. M. Auld and A. Hantzsch.—The compound formed by dissolving mercuric oxide in an alkaline aqueous acetone solution is characterised by its solubility in water. It has never been thoroughly investigated, because it readily passes into an amorphous form insoluble in water, having the empirical formula $2C_3H_6O \cdot 3HgO$. If the soluble form is rapidly freed from hydroxyl ions, it is fairly stable and yields well characterised haloid salts. With haloid acids it gives mercuric salts of the formula

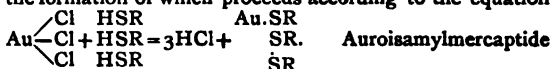
$\text{C}_6\text{H}_{10}\text{Hg}_3\text{O}_3\text{X}_2$, and therefore contains two hydroxyl groups combined with $\text{Hg}:\text{C}_6\text{H}_{10}\text{HgO}(\text{HgOH})_2$. With bromine it yields asymmetric dibromacetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CHBr}_2$, and is therefore a derivative of asymmetric dimeric acetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{HgOH})_2$. Finally, it is indifferent towards hydroxylamine and phenylhydrazine, and hence contains no intact ketone carbonyles. Thus the compound is probably trimeric diacetone hydrate, and the structural formula is—



Grignard's Reaction.—Adolf Baeyer.—It is generally necessary when acting with magnesium on benzene bromide or iodide and analogous compounds to render the magnesium active by the addition of some iodine, in order to enable it to act upon the organic compound. With bromine or iodine alkyl, magnesium acts at once in ethereal solution. The author has now found that magnesium becomes capable of acting on the benzene derivatives without the addition of iodine or alkyl compound, if the finely divided metal is previously coated with a thin layer of magnesium iodide. The magnesium thus treated forms a dull grey powder, which becomes brown in time, and must be carefully protected from moisture. This active magnesium gives off a gas with water. With methyl alcohol gas is evolved energetically, until all the magnesium is dissolved, and a white mass, probably consisting of magnesium methylate, is left behind. Ethyl alcohol acts less energetically, and amyl alcohol not at all. The active magnesium has no action upon benzene chloride, but reacts very violently with benzene bromide. It also reacts with all iodated anilines and dimethyl anilines, most energetically with the ortho- and least with the para-compounds.

Cellulose.—H. Riesenfeld and F. Taurke.—The best solvent for cellulose is a solution of copper oxide in ammonia, but the authors found that a specimen of pure cellulose was quite insoluble in this reagent. On the other hand, a solution of copper carbonate in ammonia was found to be a very good solvent (prepared by adding the calculated quantity of sodium carbonate to an aqueous solution of copper sulphate, filtering off the green precipitate, washing and dissolving in concentrated ammonia). The cellulose dissolved by this reagent is precipitated by salts, acids, water, and alcohol. Iron, nickel, and tin have no effect upon the solution, while zinc, cadmium, aluminium, and lead precipitate both copper and cellulose. When the solution is heated, a brown precipitate separates. This was dried and analysed, and it was found that on treatment with dilute acid the copper goes into solution, and the cellulose remains behind quantitatively. Analysis shows that the percentage of copper present in the precipitate is nearly constant, while the percentage of cellulose varies somewhat, possibly owing to difficulties attendant upon the drying process. It is decomposed by acids and is soluble in ammonia.

Compounds of Gold with Organic Radicles containing Sulphur.—F. Hermann.—The author has investigated the properties and preparation of auromeraptide, the formation of which proceeds according to the equation



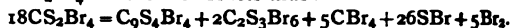
and aurobenzylmercaptide are prepared similarly. With dibenzyl sulphide gold chloride forms colourless crystalline needles. Under no circumstances is a compound yielded which contains more than one molecule of sulphur to an atom of gold. The compound has the composition $\text{AuS}(\text{C}_7\text{H}_7)_2\text{Cl}$. It is difficultly soluble in ether and cold alcohol, easily soluble in boiling alcohol, and almost insoluble in carbon tetrachloride. The best solvent is chloroform. The compound is dimorphic. From hot supersaturated solutions, or if it is precipitated from its solution

by the addition of indifferent reagents, it separates out on cooling in the form of needles, while on slow evaporation of solutions at ordinary temperatures large rhombohedral-looking crystals are obtained. Both modifications behave similarly on heating—they melt at 122° , metallic gold being split off. The compound is not very stable; it can hardly be re-crystallised without giving off ammonia. In all reactions it behaves as an aurous compound, and its constitution appears to be shown by the formula $\text{Cl.Au:S(C}_7\text{H}_7)_2$ or $\text{Au.S(C}_7\text{H}_7)_2\text{.Cl}$. With aqueous ammonia and ether it dissolves rapidly, forming two layers. The upper one, on evaporating off the ether, leaves pure dibenzyl sulphide. If the aqueous layer is filtered and evaporated over sulphuric acid, as the ammonia gas escapes white spheroidal microcrystalline concretions separate off at the surface of the liquid, and these finally form a layer all over the liquid, so that the evaporation of the water is stopped until the layer is broken through. Finally, a chalky crust is left behind, appearing slate-grey on the surface. The composition corresponds approximately to that of auroamine chloride, $\text{Au.NH}_3\text{.Cl}$. A compound $\text{AuCl}_2\text{S(C}_7\text{H}_7)_2$, dichlorauridibenzyl sulphide, is prepared by mixing ethereal solutions of two molecules of gold hydrochloride and three molecules of dibenzyl sulphide. It is an auric compound, and with alcoholic ammonia solution yields a precipitate which, when dry, explodes slightly on heating.

Decomposition of Casein by Ozone.—C. Harries.—Casein was dissolved in $\frac{1}{2}$ N caustic soda and exposed to the action of ozone until dilute hydrochloric acid gave no precipitate of unchanged casein. The solution thus obtained contained no hydrogen peroxide, and only feebly reduced Fehling's solution. After standing, the ozonised solution developed a characteristic smell of melted sugar. The author then endeavoured to isolate the sugar substance by means of phenylhydrazine. An osazone was thus formed, which contained almost all the phosphorus of the casein, and possessed acid properties, reduced Fehling's solution, like the osazone of milk-sugar, but was difficultly soluble in water. When the ozonised solution was treated with lead acetate, a white precipitate resulted, from which, on treatment with sulphuretted hydrogen, a white substance soluble in water could be obtained, containing nearly 2 per cent phosphorus, and over 40 per cent oxygen, while the nitrogen amounted to 5 to 7 per cent. The substance had an acid reaction, gave no biuret reaction, and no precipitate with phosphorus tungstic acid. When its neutralised aqueous solution was warmed with phenylhydrazine hydrochloride and sodium acetate, and normal hydrochloric acid was added, the same yellow osazone was obtained as was produced directly from the ozonised liquid.

Action of Sulphur on Carbon Tetrabromide.—A. von Bartsch.—An intimate mixture of one molecule of dry carbon tetrabromide with two molecules of flowers of sulphur was heated in a fractionating flask on an oil-bath, and the products were collected in a cooled vessel. The mixture melted at 100° – 110° , and a reaction began to occur at 150° – 160° . At 180° – 195° a liquid (first yellow and then dark red) distilled over. The residue in the flask was dark blue. This was purified by shaking with ether and heating with alcohol, and dried at 100° . The blue product was insoluble in most solvents, with the exception of fused phenol, with which it readily gave a blue solution. It dissolved in hot concentrated sulphuric acid very readily, and fairly easily in concentrated nitric acid and hydrochloric acid. Aniline appeared to act upon it chemically. Analysis showed that the composition is $\text{C}_9\text{Br}_4\text{S}_4$. Probably the compound belongs to the aromatic series, in which case the sulphur forms the chromophore group .S.S., and the compound is thus chromogenic. The distillate was then examined. It was heated on a water-bath, when more than half distilled over, giving a liquid which is not a single compound, but probably a mixture of free bromine and carbon disulphide, containing also small quantities of bromine. From the residue in the boiling flask an oil could be extracted from

which a crystalline mass of carbothiohexabromide, $\text{C}_2\text{S}_3\text{Br}_6$, could be separated. Thus the products of the action of sulphur on carbon tetrabromide are the blue compound $\text{C}_9\text{S}_4\text{Br}_4$, the white crystalline compound $\text{C}_2\text{S}_3\text{Br}_6$, carbon tetrabromide, carbon disulphide, and bromine, and also, according to all indications, large quantities of bromine sulphide. Probably first of all CS_2 and Br are formed, which partly go over as such, and partly combine to CS_2Br_4 . This then reacts thus:—



The tetrabromide is partly decomposed to bromine, bromine sulphide, and carbon, which latter is contained in the blue residue. The carbothiohexabromide and carbon tetrabromide dissolve in the bromine sulphide or bromine, and go over at a relatively low temperature. If the bromine is distilled off the liquid boils at a higher temperature, at about the boiling-point of bromine sulphide. This liquid dissolves in ether, from which the carbothiohexabromide may be precipitated by alcohol, and the carbon tetrabromide by water in the filtrate.

Preparation of Perchloroethane.—K. A. Hofmann and E. Seiler.—The authors have found that aluminium amalgamated superficially, when treated with carbon tetrachloride at 70° , yields aluminium chloride, considerable heat being evolved, and large quantities of hexachlorethane are simultaneously formed. To avoid loss of material the reaction is allowed to proceed to its termination, the brown liquid is poured off and mixed with twice its volume of ice-water. The excess of carbon tetrachloride is then distilled off. At 100° the perchlorethane begins to go over with the water-vapour. By shaking with ether the perchlorethane is separated from the water, and it is dried and evaporated *in vacuo*. The preparation has the characteristic camphor smell, rhombic crystalline form, and sublimation-point of pure perchlorethane, and the authors also determined its percentage of chlorine, which agrees with that of C_2Cl_6 . With chloroform amalgamated aluminium reacts in such a way as to form carbon, even if the chloroform is present in excess. Hydrogen is evolved, and aluminium chloride goes into solution; the latter then decomposes the excess of chloroform, giving off hydrochloric acid. Roughly speaking, 50 per cent of the chlorine in aluminium chloride escapes as hydrochloric acid from the chloroform solution.

MISCELLANEOUS.

Appointment.—Dr. H. A. D. Jowett, who for nearly ten years has filled the position of Senior Research Chemist on the staff of Dr. F. B. Power, Director of the Wellcome Chemical Research Laboratories, is about to leave that position, in consequence of his appointment as chief of the Experimental Department at the works of Messrs. Burroughs, Wellcome, and Co., Dartford, Kent.

MEETINGS FOR THE WEEK.

WEDNESDAY, Nov. 1st.—Society of Public Analysts, 8. "A Rapid Method for the Determination of Tin in Copper-tin Alloy" and "Water from the Simpson Tunnel," by A. G. Levy. "Dila Oil" and "Surin Fat," by J. Lewkowitch. "Determination of Oxygen in Copper," by L. Archbutt.

THURSDAY, 2nd.—Chemical, 8.30. "Solution and Pseudo-solution—Part V. Some of the Arsenious Properties of Arsenious Sulphide and Ferric Hydrate," by E. Linder and H. Picton. "The Molecular Conductivity of Water," by P. Blackman. "Stereoisomerism of Substituted Ammonium Compounds," by H. O. Jones. "Influence of very Strong Electro-magnetic Fields on the Spark Spectra of Ruthenium, Rhodium, and Palladium," by J. E. Purvis. "The Fluorides of Selenium and Tellurium" by E. B. R. Frideaux. "Constitution of Glutamic Acid," by J. F. Thorpe. "Some Alkyl-derivatives of Glutamic Acid and of 2:6-Dioxypyridine," by H. Bares and J. F. Thorpe. "Formation of β -Methylglutamic Acid and of $\alpha\beta$ -Dimethylglutamic Acid," by F. V. Darbishire and J. F. Thorpe.



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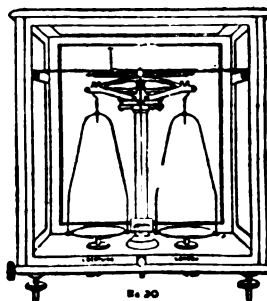
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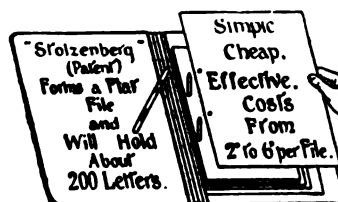
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ON A RADIO-ACTIVE SUBSTANCE DISCOVERED IN THE TRANSVAAL AND EXPERIMENTS CONNECTED THEREWITH.*

By R. LEWIS COUSENS, M.Inst.E.E.

THE discovery of a radio-active substance of which this paper forms the subject-matter, was made last year by means of certain electrical instruments which I have devised for field-work for the discovery of minerals. When examining a sample away from a certain deposit for the purpose of finding out of what it consisted, I noticed on removing the sample, which was in an ordinary sample bag, that my instruments were still affected, thus showing that there was induced radio-activity on the ground where the sample had been placed. The radio-active ore, where found, was in the form of alluvial, consisting principally of pot clay, with silica of coarser grain, and on washing this off and concentrating, I found a heavy deposit of black iron sand and other minerals, the nature of which will be more fully alluded to hereafter.

The concentrating appliances I had with me at the time were of the crudest description; a small zinc bath was used for puddling the ore; the residues were then washed over a blanket, and what we caught thereon was retained and panned in order to get rid of the remaining silica as far as possible; the residuum (the proportion of which to the crude ore was about one-fifth of 1 per cent) I regarded as concentrates.

The previous experiments were then repeated with the concentrates, a certain portion being placed in glass bottles, which were corked. I found that the ground on which the bottles were placed was made radio-active by induction, whilst if the concentrates were put into a tin there was only a very small amount of induced radio-activity on the ground underneath, thus proving that tin cuts off most of the energy that causes this induced radio-activity. From this and other experiments it appears that this induced radio-activity is not caused directly by the emanation coming in contact with the ground, as the bottles were tightly corked, but by one of the three classes of rays that are given off. By this is meant, of course, those known as α -, β -, and γ -rays, one class of which is evolved by all radio-active substances, whilst radium and thorium from one of their products emit all three.

I made rough experiments on the spot with regard to the power that different substances have of absorbing and retaining this induced radio-activity, and found that iron, lead, tin, zinc, and copper do not retain this induced radio-activity for much longer than an hour; silver, gold, and nickel for several hours; whilst platinum absorbs and retains the radiations for more than twenty-four hours after the bottle of concentrates experimented with has been removed.

On my return to Johannesburg, experiments were made to determine whether a photographic plate would be affected. A bottle of concentrates was placed on top of a key, the latter being on the photographic plate, the whole being placed within a light-tight box in a dark room. On developing the plate in the usual manner, after about twenty-four hours' exposure an image of the key was discernible; it was by no means perfect, but still it was there. These photographic experiments were continued with varying degree of success; sometimes very good radiographs were taken, at others no image appeared on the

plates, although in the majority of cases in which no image was impressed the whole plate was fogged, as if the rays of light had penetrated through all the metallic objects placed thereon.

This was proved to be frequently the case, as with two radiographs, successfully taken, of a magnet and two brass wheels, a soft iron key placed, in the one case, on the two brass wheels, and in the other across and on top of the poles of the magnet, the rays of light have penetrated through the soft iron key, the brass wheels and the edges of the magnet underneath being clearly outlined.

In all these earlier experiments the time of exposure of the plates was from twenty-four hours to three days, within a light-tight box in a dark room, and the concentrates were kept either in the containing bottle or were, immediately preceding the experiment, poured out on photographic black paper, or one or more layers of brown paper placed on top of the objects to be taken.

Experiments were also undertaken in a private laboratory, where photographic plates were affected through mica-sheet, several thicknesses of black photographic and brown papers, and aluminium plate.

Further, a tube containing a solution of iodoform and chloroform was placed in the middle of a heap of concentrates, and allowed to stand in the dark for about twelve hours, at the end of which time it was found that the colour had changed from a light yellow to a deep claret, due to the liberation of iodine.

The bottle in which the concentrates used for the last experiment were kept was left uncorked for several days, and on trying the electroscope experiment (noting the time the leaves take to collapse, by ionisation of the air between two plates, with the material under test) no result followed; the bottle was then corked for two weeks, and the experiment repeated, when the leaves collapsed in sixteen minutes. A Crookes spinthariscopes containing a small quantity of radium collapsed the leaves in four and a-half minutes, and the same result was brought about by atmospheric leakage in half-an-hour, owing to the fact that at the time wet weather prevailed.

Another sample of concentrates that had been exposed to the atmosphere at first also gave no results, but on grinding in a mortar and then placing on the test plate, the leaves collapsed in fourteen minutes.

In the meantime samples of the concentrates had been sent both to Cape Town and London for examination, and in each case the reply was received that no radio-activity could be found therein.

These replies, in face of the results that had been already obtained, were distinctly disappointing; I therefore determined if possible to carry out the work of research in a more extended manner, and accordingly applied to the Council of the Transvaal Technical Institute for permission to use their laboratory at the Institute, and my thanks are due to these gentlemen and to Professor Hele-Shaw for granting me every facility for so doing. My thanks are also due to Professors Dobson, Young, and Wilkinson for their advice, material help, and assistance when carrying out the various experiments.

The tests so far made pointed to the fact that in order to be fairly certain of obtaining results, the concentrates should be kept in a closed vessel, either during or at least preceding the various experiments, which implied that there was some very opaque substance or substances mixed with the radio-active matter, choking to a large extent the rays given out, and perhaps preventing the free generation of the emanation.

It appeared to me that the results so far obtained were caused by the rays given out by the small amount of emanation which is evolved, or its products, and which are retained if the concentrates are kept within a closed vessel, whereas if the concentrates are exposed to the atmosphere, the emanation that is evolved is dissipated in the air as fast as it is produced, and therefore results are unlikely to follow.

If this theory is correct, viz., that the results obtained

* A Paper read before the British Association (Section B), South Africa Meeting, 1905.

were caused by the emanation that is evolved, there is also the fact to be considered that the condition of the emanation itself is constantly changing, which fact was brought forward by Professor Rutherford* in the Bakerian lecture, in which he states that the emanation changes successively into at least five different states or elements, termed radium A, B, C, D, and E, and that when in state C it gives out all three different classes of rays; when in state B it is rayless; when in states A and E it gives out α -rays only, and when in state D it gives out β - and perhaps γ -rays only. The stability of the atom, or the periods of time it takes for each product to be half transformed, is computed by him as four days from emanation to radium A; from radium to radium B, three minutes; from radium B to radium C, twenty-one minutes; from radium C to radium D, twenty-eight minutes; and from radium D to radium E, about forty years.

It may be asked, if the above theory is correct with regard to the condition of the concentrates described, why the same does not apply to the radio-active ore, viz., uranium or pitchblende found in Europe, in which there is a considerable amount of opaque minerals, but which (I believe I am correct in making this statement) will always give photographic results if a plate is exposed thereto for sufficient time?

The reply to this is that, apart from any radium that may happen to be in the ore of uranium or pitchblende, there are other radio-active substances present, and also the ore itself is radio-active, as it gives out certain classes of rays capable of affecting a photographic plate, whilst with the concentrates from the deposit described, there is only (so far as my present research goes) one kind of radio-active matter contained.

The European ore contains radium in very small quantities—according to Professor Curie about $\frac{1}{4}$ grains per ton; the question arises would this small amount have been sufficient to have been noticed if the other radio-active substances were absent; or, in other words, would radium have ever been discovered under these conditions?

Professor Curie has stated†:—

"The radio-activity of a complex substance is generally greater the larger the proportion of the radio-active metal in the compound. Certain ores of uranium, as pitchblende, chalcocite, &c., have, however, a radio-activity superior to that of metallic uranium. We therefore questioned whether these minerals might not contain in minute proportion some substances still unrecognised and far more radio-active than uranium, and we searched by chemical methods for the hypothetical substances, always guided by the radio-activity of the substance treated."

Madame Curie, in her work on "Researches on Radio-active Substances" (Paris, 1904), gives comparative results of samples of various radio-active ores by measuring the current of electricity passing between two plates 3 c.m. apart, the air space being ionised by the radio-activity of the sample under test, multiplied by a constant of 10^{11} .

From the table of results given in this work it appears that the radio-activity of different samples ranged from the highest, 8.3 (which was a sample of pitchblende from Bohemia), down to 0.1, the radio-activity of metallic uranium being marked as 2.3.

Now, taking as an example the figures showing the greatest radio-activity, viz., 8.3, and deducting therefrom the figures representing the radio-activity of metallic uranium, we obtain a balance of 6; this figure does not represent the radio-activity of radium alone in this particular sample, but of radium, actinium, and polonium combined, the two latter elements being also found in pitchblende. The question therefore arises what proportion of the figure 6 is represented by the radio-activity of radium

alone? This is not given in the work referred to, but it can doubtless be arrived at by mathematical deduction from further experimental results; taking it, however, at 50 per cent of 6 = 3, it will be seen that with the samples showing the greatest amount of radio-activity, that of radium alone, owing to the small quantity present, is not much greater than that of metallic uranium. This statement, of course, does not apply when once the radium, actinium, and polonium have been concentrated down, the radio-activity of each of these three elements being far greater than that of uranium.

On the other hand also, if a quantity of radium is concentrated, its activity per unit is considerably greater than if this same quantity is distributed throughout a mass of ore. Professor J. J. Thomson has alluded to this point (*Smithsonian Report* for 1903, p. 201; reprinted from *Nature*, No. 1748, lxxvii., p. 601, April 30, 1903), stating:—

"Another point to be noted is that the radiation from a concentrated mass of radium may possibly be very much greater than that from the same mass when disseminated through a large volume of pitchblende; for it is possible that the radiation from one atom may tend to put the surrounding atoms in the unstable state. If this were so, more atoms would, in a given time, pass from the one state to the other if they were placed so as to receive the radiation from their neighbours than if they were disseminated through a matrix which shielded each radium atom from the radiation given out by its neighbours."

This statement also implies that the life of radium, or the stability of its atom, depends to a large extent upon whether it is concentrated or not, a point alluded to later on in this paper.

The conclusion to be arrived at is:—That the discovery of radium might not have been made at all if this element had not been combined with other radio-active substances.

It was on the assumption that the above views were correct that I commenced the experiments at the Transvaal Technical Institute.

The first point, therefore, that required investigation was to find out as far as possible the exact nature of the constituent parts of the concentrates; these were microscopically examined for me by Professor Young, who informed me that they consisted of silica, zircon, rutile (or oxide of titanium), and iron compounds in the form of magnetite and ilmenite, with perhaps a very small quantity of other metals. In order to find out if possible whether the concentrates were as opaque as I had imagined, I obtained a Crookes spintharoscope, and buried the carrier on which the small portion of radium chloride is fixed in the concentrates, at the same time covering as small a proportion of the fluorescent screen as possible. I found when I had done this that there was no fluorescence on the screen apart from that produced by the screen itself, proving that there was some very opaque matter present.

The question then arose which was the most opaque substance of those mentioned above? Professor Rutherford has partially dealt with this subject in one of his papers, in which he places lead and tin at the bottom of the list as being most opaque, iron about mid-way in the scale, whilst no mention is made of zirconium or titanium as having been examined. (See "Comparison of the Radiations from Radio-active Substances," by E. Rutherford, M.A., D.Sc., MacDonald Professor of Physics, and Miss H. T. Brooks, M.A., McGill University, Montreal; *Phil. Mag.*, vol. iv., No. 19, July, 1902).

I therefore next proceeded, for the purpose of examination, to divide up the concentrates by mechanical means as far possible into its constituent parts; the silica was carefully washed off by panning in porcelain dishes, the residuum dried, and the magnetite and ilmenite withdrawn by means of an electro-magnet. This left the zircon and rutile, which, being of nearly equal specific gravity, could not very well be separated mechanically.

It was found, as one would expect, that if the silica was washed clean there was no radio-activity in the same; there was a fair amount in the magnetite, considerably

* *Phil. Trans.*, A., cciv., pp. 169–219, Bakerian Lecture, "The Succession of Changes in Radio-active Bodies," by E. Rutherford, F.R.S., MacDonald Professor of Physics, McGill University, Montreal.
† *Smithsonian Report* for 1903, p. 197. Translated from a lecture delivered by Professor E. Curie before the Royal Institution of London, as printed in *The Review of Science*, Feb. 13, 1904.

more in the ilmenite, and apparently a similar amount in the zircon and rutile.

As there is probably a certain amount of titanium in the magnetite, certainly more in the ilmenite, and more still in the rutile (titanium oxide), it appears to me that in the case under review titanium is the metal which is very opaque to the rays and perhaps prevents the free generation of the emanation.

I then re-commenced a series of photographic experiments with a bottle of crude concentrates and a bottle containing the zircon and rutile for the sake of comparison.

No difference could be detected between the power of these two samples in impressing photographic negatives; an outstanding feature was that in the majority of cases the rays appeared to penetrate right through any metallic object to be photographed, and fogged the plate. For example, a radiograph of an aluminium object was taken, whilst objects of more opaque material placed on the same plate, such as gold, silver, and platinum, were not taken at all, although on repeating the experiment images of the two former were impressed on other plates. I have to add that one of the boxes in which the plates were placed during these experiments was large enough for three negatives (half size) placed horizontally edge to edge, and that frequently a dummy plate was placed therein at one end, whilst another negative was exposed to the bottle of mineral at the other. On developing the dummy plate the same came out perfectly clear, thus proving that the plates were in good condition, that there was no leakage of light from any outside source, and that the phenomena described must have been caused by rays issuing from the mineral in the bottles.

The reason of the fact that the rays frequently penetrate through metallic objects and that the plates are fogged has been explained by Madame Curie as being caused by the γ -rays. These rays are deviable in a magnetic field, so that if a very strong magnet is applied in a proper manner whilst a radiograph is being taken, a sharper image of the object is the result, caused chiefly by the γ -rays impinging on the plate; the time of exposure has, however, to be lengthened. I have not yet tried an experiment on these lines, but hope to do so on a future occasion.

My next experiments were with the electroscope. Two plates were mounted on a suitable stand within a glass globe open at the lower end, the air space between the two being adjusted by raising or lowering the bottom plate to any suitable distance within the limits of about 4 inches. The upper plate was carefully insulated from earth and electrically connected to the gold leaves of the electroscope, behind which a scale was fixed in a similar manner to the arrangements devised by Professor Curie. A sample of the zircon and rutile was placed in a tube tightly corked and laid on the lower plate. The leaves of the electroscope were charged with negative electricity in the usual manner, and collapsed very slowly; in fact only slightly quicker than the effect caused by atmospheric leakage alone. The tube was then uncorked, and the contents poured into a small copper dish placed on the lower plate; the leaves collapsed 4 degrees in five minutes, but afterwards continued to do so very slowly, proving that with the dissipation of the emanation the ionisation of the air gradually decreased.

Some iron beads obtained by smelting down some of the concentrates, using lime as a flux, gave similar results. A Crookes spinthariscopes collapsed the leaves 10 degrees in eight minutes.

A cork of paraffin-wax was then fitted into the tube, through which two wires were passed in separate apertures so as to seal it, the end of one wire being coiled near the bottom of the tube and the other just underneath the cork of paraffin-wax.

This arrangement was first tried without any mineral in the tube to ascertain if the insulation was good; the leaves fell at the same rate as that for atmospheric leakage, viz., 5 degrees in twenty-five minutes.

The substance to be tested was then placed in the tube,

to a point about midway up the tube, the end of the lower wire being buried in the concentrates and the upper wire coiled just underneath the plug of paraffin-wax, the latter being electrically connected to the leaves of the electroscope, which collapsed—

5	degrees in	10	minutes
10	"	18	"
12½	"	23	"
15	"	27	"
17½	"	30	"

The above experiment was repeated with the lower wire raised above the level of the concentrates in the tube, the leaves collapsing somewhat slower, viz.:—

5	degrees in	12	minutes
7½	"	18	"
10	"	25	"
15	"	40	"

On repeating the last experiment the following day, the tube remaining corked, the leaves collapsed 5 degrees in twenty minutes, but after slightly agitating the sample, the leaves collapsed 6 degrees in ten minutes and 7 degrees in fifteen minutes. In order to increase the surface area of the material under test, the tube being rather small in diameter, a cavity was made in a block of paraffin-wax, to the bottom of which a copper coin was fixed, connected with a wire through a hole bored at the side of the block with a larger coin on top of the cavity electrically connected with the leaves of the electroscope.

As there was a large amount of atmospheric leakage, it being a wet day, careful tests were made as to the rate of fall of the leaves, putting mercury into the cavity, so as to reduce the height of the air space by about one-half. The leaves collapsed—

2½	degrees in	5	minutes
4	"	8	"

The mercury was then removed, and a quantity of concentrates poured into the cavity which occupied the same space as that of the mercury in the previous test. The leaves collapsed—

2½	degrees in	3	minutes
4	"	5	"
5	"	6	"
6½	"	8	"

A Crookes spinthariscopes of a somewhat larger size than that used in previous experiments collapsed the leaves—

10	degrees in	5	minutes
12	"	6	"

On repeating the previous experiment the following day, the leaves collapsed—

10	degrees in	6½	minutes
20	"	16	"

without previously agitating the material; after doing so the leaves collapsed—

10	degrees in	3	minutes
30	"	16	"

The test for atmospheric leakage on this day was 5 degrees in eight minutes.

On testing some ilmenite which, as alluded to before, was radio-active, and had been extracted by an electromagnet, the leaves collapsed—

10	degrees in	5	minutes
20	"	15	"

Two small samples of pitchblende and polonium used with a scintilloscope gave negative results. As, however, they were enclosed in glass cases which I did not care to disturb, the test was not a comparative one, and I would here also add that, apart from any radium that may happen to be present in pitchblende, neither the latter mineral nor polonium give off any emanation, and therefore there

would be no ionisation of the air from either of these two elements except by the rays emitted by these minerals.

My next experiments were with a mirror galvanometer.

The constant of this galvanometer was 0.0000000122 ampère per degree deflection on scale. On testing a sample placed in the cavity in the block of paraffin-wax before referred to, and applying a steady voltage of 100 volts from the accumulator battery of 50 cells, there was practically no deflection of the galvanometer, but on testing the sample, which had been kept for some days in the test-tube fitted with the paraffin plug, as before described, the galvanometer showed 5 degrees deflection on the scale.

The current therefore passing was $5 \times$ constant of the instrument = 5×0.0000000122 ampère, and the resistance of the ionised air was 1.64×10^{10} ohms.

The above result multiplied by Madame Curie's constant of 10^{11} is 610; this is so greatly superior to any effect obtained by her with any crude sample of ore that I think the cause must be partly due to—

- a. The fact of the electrodes (copper wires) in the tube being closer together than the distance between the plates (3 c.m.) of the air condenser used by Madame Curie.
- b. The air between the top of the mineral and the plug on top of the tube was perhaps partially laden with dust derived from the mineral under test; this would increase the conductivity of the air space and give an exaggerated result.

When repeating this experiment I intend to place some cotton-wool on top of the mineral to prevent as far as possible any dust rising to the top of the tube.

The experiment of ionising the air between the secondary terminals of an induction-coil was next tried. The secondary terminals were placed apart so as to be beyond the sparking distance: on uncorking a bottle containing the minerals, sparks passed between the secondary terminals, which, however, after a time ceased, thus proving again that the emanation ionised the air, but with the dissipation of the former the ionisation decreased.

The conclusion to be arrived at from all these experiments is to confirm my previous idea, viz., the results obtained are due, principally at least, to the small amount of emanation that is given off, or its products, and therefore it is necessary to keep the concentrates within a closed vessel, at least until the experiments are proceeded with; also that fine grinding and agitating the ore causes more emanation to be evolved, thus giving improved results.

Unless these precautions are taken, results with the raw concentrates, with the usual tests, are unlikely to be obtained, at least until the opaque matter has been removed.

(To be continued).

THE VISCOSITY OF LIQUID MIXTURES AT THEIR BOILING-POINTS.*

By Dr. ALEX. FINDLAY.

ALTHOUGH a considerable amount of work has been done on the viscosity of mixtures of two liquids, comparatively few generalisations of importance have been obtained. In some cases it was found the viscosity of a mixture varied comparatively little from that calculated according to the mixture formula, while in other cases, more especially when one of the constituents of the mixture contained the hydroxyl group, marked deviations from the mixture law were obtained; the viscosity-composition curve showing a maximum or minimum point. The maximum or minimum point, further, was found to shift with the temperature at which the viscosity was determined. We are therefore met by the difficulty, here as in many other cases, of

deciding the temperature at which the determinations of the viscosity should be carried out.

So far these determinations have been carried out at one temperature throughout the whole series of mixtures, but as these investigations have been only partially successful, it was decided to determine the viscosity of a number of binary mixtures at the temperatures of the boiling-point of the respective mixtures. In this way it was thought some relationships might be discovered with other physical constants, and it was anticipated that a general relationship would be found more especially between the viscosity-composition curve and the boiling-point-composition curve. This anticipation has been only partially realised in the small number of cases so far investigated, viz., benzene-carbon tetrachloride, benzene-alcohol, acetone-chloroform, benzene-methyl alcohol. As a much larger number of mixtures must first be examined before general conclusions can be drawn, it will suffice at this stage to draw attention to the line along which the investigation is proceeding.

ALTERNATE CURRENT ELECTROLYSIS.*

By ERNEST WILSON, M.I.E.E.,
Professor of Electrical Engineering, King's College, London.

(Concluded from p. 200).

Iron.

Ferrous Sulphate (strong).—The iron plates were cut from good transformer plate and cleaned with emery paper, thereby presenting a bright but not perfectly smooth surface. Alternating currents have a marked effect upon iron in this solution. Experiment 13 was made first, and it was found that the plates lost 0.000462 gm. per sq. c.m. per hour. Without changing the solution, which during the experiment had taken up 2.4 grms. of iron, the plates, after being dried and rubbed with wash-leather to remove the surface oxide, were again inserted, and Experiment 14 made. The frequency was the same in each experiment, but the maximum coulombs were increased from 0.00956 to 0.0346. The result was to dissolve only 0.000457 gm. per sq. c.m. per hour, as compared with 0.000462 in Experiment 13, the solution again going up in density. Experiments 15 and 16 were then made with fresh solutions, but using tap-water instead of distilled. A small quantity of H_2SO_4 was added, to delay oxidation and to correct the calcium salts in the water. The result shows that 0.00389 and 0.00445 grms. per sq. c.m. per hour were thrown down, and these are roughly eight-fold the weight thrown down in Experiment 14, although the frequency and maximum coulombs are the same. The presence of some free acid in Experiments 15 and 16 may be accountable for the high figures obtained. A test sample in the solution of Experiment 13 lost 0.4 per cent of its weight in fifty-eight hours, as against 2.5 per cent of the submerged portion in seven hours in the experiment. There is considerable electrolysis. Experiment 17 was then made. In it the solution was made with distilled water acidified to the extent of 1 c.c. of H_2SO_4 in 2000 c.c. of water to delay oxidation, and nearly saturated with pure $FeSO_4$. Comparing Experiments 13 and 17 for the relation between grms. dissolved and maximum coulombs per half period, we find that 0.000229 gm. per sq. c.m. per hour should be dissolved if the relation held, as against 0.000462 observed at the higher frequency. Similar results were obtained in the cases of lead and zinc in dil. H_2SO_4 . Lead and iron give, roughly, the same ratio between the observed and calculated weights. It should be remembered that in these experiments not the whole of the plate is submerged in the solution, and there may be some additional effect at the surface of the liquid where it joins the plate.

The curve obtained in Experiment 13 between the exploring iron electrode and one plate is numbered 13 in

* Abstract of a Paper read before the British Association (Section B), South Africa Meeting, 1905.

* A Paper read before the Faraday Society. July 3, 1905.

Experiment.	Metal.	Solution.	Duration of test, in hours.	Frequency.	Density of solution.		Temperature of electrolyte C.		R.M.S., amperes per sq. c.m.	Maximum coulombs per half period.	Weight of plates, in grms.		Difference in weight of two plates after rinsing in water and drying.	Difference in weight after rubbing with wash-leather.	Average grms. per hour after rinsing in water and drying.	
					Before.	After.	Before.	After.			Before.	After.				
1.	Lead ..	H ₂ SO ₄ (dil.) ..	15	21.5	1050	1049	17.0	—	0.0236	0.0394	401.019	397.065	-30.2	—	0.00629	(a)
2.	Do. ..	Do.	15	92.5	1050	1049	17.5	—	0.0236	0.0094	398.977	402.190	-16.5	—	0.00344	(b)
3.	Do. ..	Do.	8	92	1050	1036	21	32	0.0847	0.0335	389.900	393.105	-87.9	—	0.03330	(c)
4.	Zinc (amalgamated).	Do.	14½	25.5	1038	1068	17.6	19.1	0.0240	0.0345	110.58	116.67	-26.19	—	0.00530	(d)
5.	Do. ..	Do.	18	92	1038	1054	21.3	22	0.0253	0.00956	101.724	104.718	-10.72	—	0.00189	(e)
6.	Do. ..	Do.	7	92	1054	1066	19.5	27.5	0.0923	0.0346	96.647	99.073	-15.15	—	0.00695	(f)
7.	Do. ..	Do.	8	92	1048	1055	21	25	0.0889	0.0335	115.155	107.865	-4.29	—	0.00166	(g)
8.	Do. ..	Do.	32	32	1050	1058	28.5	23	0.0307	0.0334	110.120	97.935	-8.795	—	0.00337	(h)
9.	Do. ..	Do.	8	92	1050	1054	28.5	25.5	0.0889	0.0335	105.147	104.457	-2.661	—	0.00103	(i)
10.	Zinc..	Zinc chloride ..	12½	25.5	1255	1260	15	20.5	0.0247	0.0345	113.135	114.505	+0.450	—	+0.000116	(j)
11.	Do. ..	Zinc sulphate (saturated) ..	14½	25.5	—	—	—	—	0.0240	0.0345	109.860	115.237	Not taken	—	—	(k)
12.	Do. ..	Sodium sulphate ..	18	92	1100	1104	20	22.5	0.0241	0.00956	106.703	111.747	+0.186	+0.033	+0.000031	(l)
13.	Iron ..	Ferrous sulphate ..	18	92	1114	1122	21.5	21	0.0273	0.00956	64.188	61.199	-2.427	—	+0.000462	(m)
14.	Do. ..	Do.	7	92	1122	1125	19.5	29	0.0979	0.0346	63.098	59.786	-0.940	-1.101	0.000457	(n)
15.	Do. ..	Do.	8	92	1174	1186	20.6	25	0.0929	0.0335	60.085	61.330	-9.045	—	0.00389	(o)
16.	Do. ..	Do.	8	92	1174	1186	20.6	25.5	0.0929	0.0335	62.464	59.319	-11.046	—	0.00445	(p)
17.	Do. ..	Do.	8	32	1066	1102	18.5	21.4	0.0340	0.0334	55.450	56.242	-1.851	-2.012	0.000787	(q)
18.	Do. ..	Sodium chloride ..	18	92	1138	1134	22	21	0.0262	0.00956	67.108	66.242	+0.092	+0.027	+0.000017	(r)
19.	Do. ..	Do.	7	92	1134	1128	19.5	23.5	0.0929	0.0345	67.141	66.312	+0.262	+0.173	+0.000121	(s)
20.	Do. ..	Do.	8	32	1086	1090	19.5	21	0.0312	0.0334	56.977	53.295	+0.255	—	+0.000100	(t)
21.	Copper ..	Copper sulphate ..	12½	25.5	—	1105	16.25	17.3	0.0265	0.0345	138.145	140.215	-0.185	—	+0.000051	(u)
22.	Do. ..	Do.	8	92	1060	1092	19	30.5	0.1000	0.0335	134.550	136.875	-0.181	—	0.000079	(v)
23.	Do. ..	Sodium chloride ..	18	92	1138	1132	21.5	21	0.0241	0.00956	134.235	133.500	-0.165	-0.276	0.000028	(w)
24.	Do. ..	Do.	8	32	1066	1098	18.4	20.3	0.0340	0.0334	134.085	133.965	-0.653	—	0.000278	(x)
25.	Do. ..	Sodium phosphate ..	18	92	1042	1050	21.2	21.5	0.0241	0.00956	134.674	136.891	+0.009	-0.014	+0.0000015	(y)
26.	Tin ..	Protocchloride of tin ..	12½	25.5	1110	1120	16	16.8	0.0244	0.0345	123.571	119.491	-0.26	—	0.000066	(z)
27.	Aluminium	Potash alum solution (sat.) ..	2	92	—	—	20.6	98	0.1030	0.0335	—	—	Not taken	—	—	(aa)

Remarks.

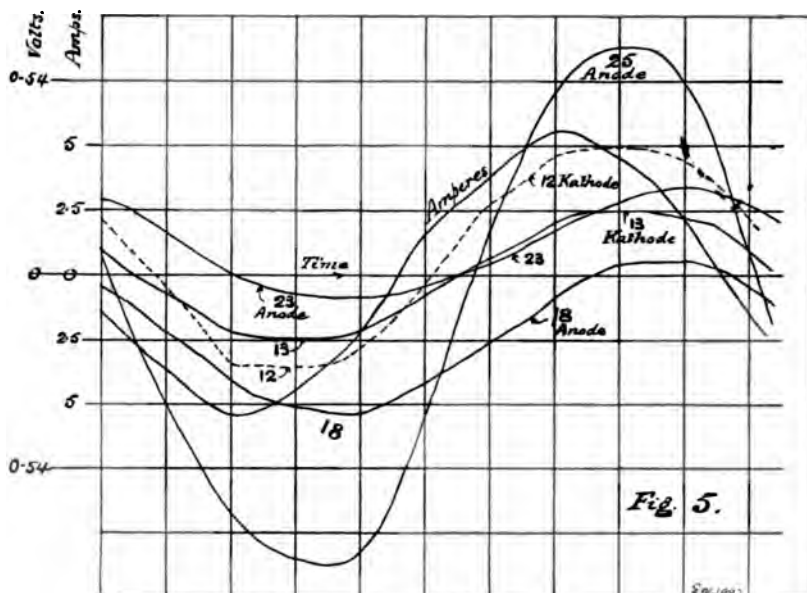
- (a) Fig. 1.
 (b) Fig. 2.
 (c) Fig. 3.
 (d) Fig. 4.
 (e) Fig. 5.
 (f) Same solution as in Experiment 5.
 (g) Same solution as in Experiment 13.
 (h) Tap water used.
 (i) Distilled water used.
 (j) Same solution as in Experiment 18.

The asterisk (*) distinguishes the one plate which was rubbed with wash-leather.

Fig. 5. Its flat top indicates that the plates are fully polarised. It is considerably out of phase with the current.

Sodium Chloride (strong).—After washing and drying, the iron plates in Experiment 18 have increased in weight, but in the solution a totally submerged test sample through which no current was passed increased weight nearly to the

Sodium Phosphate Na_2HPO_4 (strong).—In Experiment 25 the copper plates were discoloured, but not diminished in weight. In Fig. 5, curve 25 gives the potential difference between a copper exploring electrode and one plate. Comparatively this potential difference is large. If correction were made for conductivity, the phase displacements might be sufficient to show almost complete re-



same percentage, so that there is no conclusive evidence of serious electrolysis. Curve 18, Fig. 5, was obtained between the iron exploring electrode and one plate. It is very much displaced with regard to the axis of time, possibly due to the fact that the plate is easily attacked when it is an anode, thereby requiring less work during that half period. When passing from the kathode to the anode states, a full quarter period in time is required before the work done on the plate becomes positive. Experiments 19 and 20 show that an increase in the weight of the plates takes place, thereby leading to disintegration.

Copper.

Copper Sulphate (strong).—In Experiment 21 the copper plates acquire a fairly easily removable copper deposit, and show slightly diminished weight. The potential difference between a copper electrode, in the solution between the plates, and one plate is given in Fig. 4, curve 21. The curve is nearly in phase with the current, and has the same wave-form. One would expect a little electrolytic action. Comparing Experiments 21 and 22, we see that although the maximum coulombs are the same, more copper is dissolved at the higher frequency, i.e., at the higher current density. The deposited copper in Experiment 22 was not so easily removable as in Experiment 21.

Sodium Chloride (strong).—In Experiment 23 the copper plates were highly discoloured, and covered with an easily removed metallic powder. The plates show diminished weight. In Fig. 5, curve 23 shows the potential difference between a copper exploring electrode and one plate. Comparing Experiments 23 and 24, we see that much more copper has been dissolved at the low frequency than the ratio of the maximum coulombs would lead us to expect. The effect is considerable in Experiment 24, and as sodium chloride is largely met with in the earth, this experiment may have practical importance. The difference would have been a little more noticeable if the detachable deposit had been removed from the surface of the plate before estimating the loss of weight.

versibility, and thus account for the small effect observed. If this were so, the effect would be similar to what has already been observed when an alternating current is passed between platinum plates immersed in dilute H_2SO_4 (see *Proc. Roy. Soc.*, vol. liv., p. 407). Dissipation of energy still occurs owing to the decomposition of the electrolyte at the plates. Any copper phosphate formed in Experiment 25 during one-half period would be reduced during the next half period.

Tin.

Protochloride (strong).—In Experiment 26 we see that 0.26 grm. of tin have gone into solution, thereby indicating considerable electrolytic action. The curve of potential difference between the exploring tin electrode and one plate is not given in Fig. 4, as there was a possibility of the electrode touching one plate during the experiment. It indicated a very small amplitude as compared with the others.

Aluminium.

Potash Alum (saturated).—A good deal of work has been done upon aluminium in connection with alternate currents. It is known that the film formed on the surface offers considerable resistance to the electric current (see *Proc. Roy. Soc.*, vol. lxxiii., p. 329). In Experiment 27 two aluminium plates were immersed in a saturated potash alum solution, and owing to the formation of a surface layer the internal resistance gave rise to such dissipation of energy that the solution was boiling after the experiment had progressed three-quarters of an hour. The plates were very much eaten away in places, but quite bright where they had been protected by the surface layer.

In conclusion, I wish to express my thanks to Professor E. F. Herroun for valuable suggestions. Mr. D. Sheppard worked with me all through and prepared the experiments. Mr. T. Mitchell has also rendered assistance, and has worked out some of the results. To these gentlemen I tender my thanks.

OBSERVATIONS ON COLUMBIUM AND TANTALUM.

By EDGAR F. SMITH, University of Pennsylvania.

IN 1801, Hatchett, while studying minerals in the British Museum, came upon a specimen from Haddam, Conn., which attracted his attention because of its rather high specific gravity and its brilliant black colour. A portion of this material was given him for examination, with the result that he discovered in it a new metallic acid, to the metal of which he applied the name columbium. It was his earnest hope that he might obtain larger quantities of the American mineral in order to exhaustively study the new element, and it is of interest to remark that Hatchett fondly expected this material assistance from Thomas Peters Smith, a member of this Society and an enthusiast in chemical science, who on his return from England met an untimely death on shipboard.

In 1802, Ekeberg, of Sweden, while examining an unknown mineral, found that it contained a new metallic acid, to the metal of which acid he assigned the name tantalum, because "when placed in the midst of acids it is incapable of taking any of them up and saturating itself with them." Later, Wollaston (1809) strove to prove that columbium and tantalum were identical. In this he failed. The few reactions known even at that early day differentiated the new elements. About 1840, Heinrich Rose, in studying similar minerals from other localities, came to the conclusion that the American mineral contained an element absolutely different from tantalum, and called it niobium. Subsequently, owing to his inability to account for the peculiar products which he got by chlorinating a mixture of the oxide of the new element and carbon, he asserted that, in addition to niobium, there was present pelopium (1846). Later (1853), however, he seems to have arrived at the opinion that niobic acid and pelopic acid were different oxides of niobium. The first he called niobic acid and the second hyponiobic acid. Hermann also contributed to the uncertainty which surrounded the two elements (columbium of Hatchett and tantalum of Ekeberg) in that he announced the existence of ilmenium; but it was not generally accepted by chemists. Hermann, however, persisted in his declaration that it occurred along with the other two elements to which reference has been made. Von Kobell believed that he had detected dianium in allied minerals. This unfortunate state of affairs prevailed until the early sixties, when Marignac, after a careful study of a number of minerals from various localities, announced the existence in them of but two elements—the columbium of Hatchett and the tantalum of Ekeberg—and added that the confusing reactions which had perhaps led Heinrich Rose—but most certainly, Hermann and von Kobell—astray were to be explained by the presence of titanium in all tantalites and columbites. It is only fair to say that Marignac never succeeded in obtaining titanium from any one of the minerals in which, according to him, it occurred, associated together with columbium and tantalum. Indeed, in his concluding paper on columbium he frankly acknowledged that the columbium compounds which he used for the determination of the atomic weight of the metal, contained titanium, and that he knew of no method by which the latter could be separated from columbium. Marignac's conclusion was accepted by the chemists of the world as final.

When we come to examine the evidence which Marignac gives for the presence of titanium, we find that it is, practically, that the re-crystallisation of a double fluoride of columbium and potassium, supposed to contain titanium, gave rise, gradually, to a fraction which became more insoluble in water, and the molecular weight of its acid oxide approached, within ten or more units, that required by titanic oxide. It is well to bear in mind that at no time did Marignac, whose ability and keen insight one would not for a moment question, give any tests which are

ordinarily regarded as indicating titanium. He assumed it to be present on the evidence mentioned above, viz., the greater insolubility of the double fluoride and an approximate molecular weight corresponding to that required by titanic oxide. Ever since Marignac's day chemists the world over have tacitly accepted titanium as associated with columbium in columbites. They have also estimated its quantity by methods suggested from time to time. One of these methods is based on the colour reaction which titanium salts give with hydrogen peroxide. Its intensity, compared with that shown by a known amount of titanium, has been regarded by most analysts as entirely satisfactory. For the determination of the amount of titanium in columbium many methods have been proposed, but this is not the place to discuss them or their value.

As late as 1877, in the last paper published by Hermann, he announced the element neptunium, and claimed to have obtained it from the acid mother-liquors remaining after tantalum potassium fluoride, ilmenium potassium fluoride, and columbium potassium fluoride had been crystallised out. The particular mineral in which he observed it was a columbite from Haddam, Conn.: in other words, the same mineral in which columbium had been originally discovered by Hatchett.

The existence of neptunium has never been contradicted. This is probably because the majority of chemists thought that the verdict in regard to the constitution of tantalites and columbites had been given by Marignac, and that the numerous, unusual reactions of the metallic acids contained in those minerals, noted and commented upon at various times by Heinrich Rose, von Kobell, Blomstrand, and Hermann, were all due to the contaminating influence of titanium.

The two elements, columbium and tantalum, in their derivatives, have received comparatively little attention within the last quarter of a century, although at intervals attempts have been made to clear up the mystery which, in a certain sense, surrounds them. In this laboratory, several investigations upon derivatives of them have been made. These being not wholly satisfactory, about three years ago, 50 lbs. of columbite from South Dakota and 25 lbs. from Haddam, Conn., were worked up, with a view of getting an abundant supply of starting-out material; with the view, also, of studying anew the various derivatives of both columbium and tantalum. In the year 1903-1904, Dr. R. D. Hall devoted, in this laboratory, much time and labour to the double fluorides of tantalum and columbium. He made a comparative study of the reactions of the same with the reactions of titanium. His results have been published, but from an examination of them it will be observed that he was not able to find any tests, while using the double fluorides, which differentiated titanium from columbium so thoroughly that he could expect to obtain a complete separation of these two most interesting elements. It is true that he was able by precipitating potassium columbium fluoride incompletely with ammonia, to get a columbium oxide, which apparently gave no response to the hydrogen peroxide test upon its application, or to the reagent called chromotropic acid. Hence he inferred that he had eliminated the titanium from the columbium. More recent work with large quantities of material has demonstrated that in the latter cases it was impossible to entirely remove the metallic acid which gave the colour tests. It was further found that by the action of sulphur monochloride upon the oxides of columbium and titanium, corresponding chlorides were produced; but again, it proved impossible to wholly expel the titanium from the columbium by this process, notwithstanding titanium chloride is an exceedingly-volatile liquid and columbium chloride a solid crystalline body.

In the present year, we have, in this laboratory, prepared large quantities of the double fluoride of tantalum and potassium, and found no difficulty whatsoever in eliminating from it every trace of what was supposed to be the titanium double fluoride.

Having thus, at our disposal, such generous amounts of pure tantalum oxide, free from columbic oxide—in short, really pure tantalum oxide—it was determined to make a new study of the double fluorides of tantalum with the alkali metals and organic bases. This was undertaken in order to discover, if possible, why Dr. Pennington, when working in this laboratory in 1895, obtained double fluorides of tantalum and columbium with caesium, which showed these unusual formulæ, $15\text{CsF} \cdot \text{TaF}_5$ and $7\text{CsF} \cdot \text{CbF}_5$, which varied so widely from those generally followed by the double fluorides of tantalum and columbium, and were not in accord with the law proposed for double halides (*Am. Chem. Journ.*, v., 291).

At the outset it was thought that this re-investigation of the double fluorides would prove to be an easy and simple matter. But it was not long until it was seen that the discordant results of Dr. Pennington were probably due to the fact that there was more than one caesium tantalum fluoride. Indeed, the latest work done in this laboratory, by Mr. C. W. Balke, proves that there are two caesium tantalum fluorides, two rubidium tantalum fluorides, two sodium tantalum fluorides, two ammonium tantalum fluorides, and so forth, of these ratios:—

$\text{TaF}_5 \cdot \text{CsF}$	$2\text{TaF}_5 \cdot 3\text{RbF}$
$\text{TaF}_5 \cdot 2\text{CsF}$	$\text{TaF}_5 \cdot 2\text{NaF}$
$\text{TaF}_5 \cdot 2\text{NH}_4\text{F}$	$\text{TaF}_5 \cdot 3\text{NaF}$
$\text{TaF}_5 \cdot 3\text{NH}_4\text{F}$	$\text{TaF}_5 \cdot 2\text{KF}$

The existence of several such double fluorides with each of the alkali metals naturally raises the question whether these salts ought to be used for the determination of the atomic weight of tantalum, inasmuch as each salt is likely to be contaminated with smaller or larger quantities of the other, depending upon the condition or the care with which they are prepared. Marignac used potassium tantalum fluoride and ammonium tantalum fluoride in his re-determination of the atomic weight of tantalum. It would seem, from the study of the salts just mentioned, that even this skilled and careful analyst could not have been sure that he had a definite homogeneous body in the determinations which he made. Of course, if there was even a slight amount of a second salt in the salt used for the atomic weight work, it would naturally vitiate the final result. Of all the double fluorides of the alkali metals and bases with tantalum which have thus far been studied by Mr. Balke, that of sodium and tantalum, of the ratio 3 to 2, seems to be the one having some definite and most stable characteristics. We hope to re-determine the atomic weight of tantalum, but it is not probable that we shall use any one of the double fluorides of which mention has been made, although they appeal strongly because of the ease with which they can be crystallised. The uncertainty, however, as to whether they are really absolutely of one definite ratio every time that they are crystallised is uncertain. Hence they had better be abandoned in atomic weight determinations.

The question may also be asked, may not the double fluorides of columbium with the alkali metals which have been used for atomic weight purposes been contaminated with salts of varying ratios? This point will receive attention.

Turning again to columbium, it seems proper to record that, having eliminated the tantalum completely from a mixture of oxides obtained from Haddam columbite, the remaining potassium columbium oxyfluoride was crystallised a number of times from water, and also from solutions containing much hydrofluoric acid. This procedure finally gave a mother-liquor that was decidedly acid. A metallic acid remained in this mother-liquor. According to Hermann, in his communication of 1877, this acid should be neptunic acid. Therefore, the acid mother-liquor was treated as directed by Hermann, namely, it was evaporated, the residue was dissolved in water, and the boiling solution precipitated with an excess of caustic soda. The precipitate, after the liquid had become cold, was filtered out, pressed thoroughly from adherent water, and then

boiled with twenty-five times its own weight of pure water. Everything dissolved. The solution was perfectly clear. On cooling, there separated from it the beautiful needle-like crystals of sodium columbate. According to Hermann, the precipitate which was collected, pressed out and then boiled with water, should, if neptunium were present, have left a slimy mass, insoluble in water. This, Hermann said, was sodium neptunate. It should be observed that our experiments were made with the final acid liquors obtained from the double fluorides present in columbite from Haddam; further, that we proceeded in strict accordance with the directions of Hermann, and having done all this, did not obtain a gelatinous mass which might have been sodium neptunate. In Hermann's communication, to which reference has been made so frequently, he lays great stress on the fact that the distinguishing reaction of neptunium is the beautiful golden-yellow colour which sodium neptunate imparts to a salt of phosphorus bead in the *reducing flame*. It is needless to add that we tried on different occasions to find neptunium, according to the directions of Hermann; but our search was fruitless. On one occasion, however, we obtained a mass, not great in amount, which, in the inner blowpipe flame, did impart a yellow colour to the salt of phosphorus bead, but more careful examination of this residue demonstrated that it contained tantalum, iron, and some columbium. The intense golden-yellow colour, which was so strongly emphasised by Hermann, we could not get; so that it is very probable that neptunium, like ilmenium and the other metals announced from time to time as present with columbium and tantalum, must really be placed in the list of defunct elements. It has not been our wish to bury this candidate for elemental honours. Indeed, we would have been only too glad to have found the evidences of its existence, and to have confirmed the observation of that earnest and sincere student of chemical science, who, in his tireless labours, frequently felt confident that he had fallen upon the cause of the varying results observed with columbium and tantalum.

In this connection it may be added that, having freed the tantalum and columbium oxides as thoroughly as possible from ordinary contaminations, the problem of removing tungsten and tin confronted us. After much experimentation, we found that the certainty of the removal of these impurities could only be had by fusing the tantalum and columbium oxides with sodium carbonate and sulphur. It is true that small quantities of tantalum and columbium will be lost, being carried along with the tungsten and tin, but as we were seeking a method of purification and not a separation, we adopted this course. It is the one which was pursued by Heinrich Rose. Our own experience leads us to say that the removal of tungsten and tin from columbium and tantalum oxides cannot be realised by digestion with ammonium sulphide. Indeed, not only did we find the fusion with the sodium carbonate and sulphur necessary, but that working in large quantities of material, as in our case, two and three refusions with these reagents were found necessary. Another point of interest in connection with the purification of the tantalum and columbium oxides may be mentioned. It has frequently been said that in crystallising out the double fluorides of these metals, if titanium be present with them, it will be found in the potassium tantalum fluoride. We have encountered no difficulty in getting potassium tantalum fluoride perfectly free from what is supposed to be titanium by one or two crystallisations. It has been assumed that, as potassium titanium fluoride is rather insoluble in water, it would naturally go with potassium tantalum fluoride. This, however, seems to be an incorrect observation. It masses with the columbium potassium fluoride; at least the element which gives the yellow colour with hydrogen peroxide, or a rose-red with chromotropic acid, is always found associated with the columbium. How to free the columbium from titanate acid we do not know. We are in precisely the same position as that of Marignac, notwithstanding we have probably made greater efforts than he to

remove it from the columbium. It is this point in our investigation upon which we have been continuously at work for the last year. We have tried fractional precipitation with ammonia water, fractional crystallisation of the double fluorides, fractional chlorination of the oxides in the presence of carbon and the action of numerous organic bases, without finding any way of effecting a separation. Indeed, the separation of columbium and titanium is a problem which the analyst has not solved up to the present. As remarked, it has received and is receiving our daily attention. Once having achieved this result, and having definitely determined the character of the colour-giving metallic acid, or proved it to be titanium, without any further doubt, we then hope to subject the purified columbic oxide to a searching review in all its derivatives, just as we are now doing with the compounds of tantalum. In anticipation, it may be said that there are some most interesting complexes of tungstic acid with tantalum oxide, and also of tungstic acid and columbic acid. These are under study at present. These complexes, also, have brought analytical problems that are most puzzling. Yet our progress with them leads us to hope for a separation and a satisfactory solution of the same.

Some attention has likewise been given to per-tantalates and per-columbates. It would not be the least surprising to find these derivatives answering admirably for atomic weight work.—*Proceedings of the American Philosophical Society*, 1905, xlv., p. 151.

NOTICES OF BOOKS

Physical Chemistry and its Applications in Medical and Biological Science. By ALEX. FINDLAY, M.A., Ph.D., D.Sc. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THESE lectures, which were delivered before the University of Birmingham, were intended specially for the benefit of students of medicine and biology, to give them an elementary introduction to the application of physical chemistry to these sciences. The lectures deal with elementary conceptions regarding osmotic pressure, the theory of ionisation, and the study of the disinfective and toxic action of ions, the permeability of membranes and adsorption catalysis, and colloidal solutions. Thus it will be seen that they touch upon a considerable range of subjects, and cannot be expected to do more than point out the leading features to be noticed; considering all things, the small amount of chemical knowledge the audience might be supposed to possess, and the limited time at the lecturer's disposal, he has been wonderfully successful in imparting a considerable amount of valuable information in a lucid and interesting manner, and the book will be of great use to the biologist who wishes to become familiar with the applications of physical chemistry to his branch of science, and to whom the author looks for advances as regards the solution of biological problems.

Soils and Fertilisers. By HARRY SNYDER, B.S. Second Edition. Easton, Pa.: The Chemical Publishing Co. 1905.

THE changes made during the revision of the text of this work, and the extensive and important additions, have altered its scheme to such an extent that a change of title seemed advisable. As it now stands it gives a full account of the chemistry of soils, the use of all kinds of fertilisers, and the food requirements and rotation of crops, together with outlines of the laboratory practice necessary to illustrate the text, and it appears all that could be desired for the use of those who, without aspiring to the acquirement of a large

amount of scientific knowledge, wish to become acquainted with the chemical principles underlying the art of the farmer, and to be capable of dealing in an intelligent spirit with the problems with which he is confronted, without falling back on mere rule-of-thumb methods.

Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie. ("Modern Conceptions in the Sphere of Inorganic Chemistry"). Braunschweig: Friedrich Vieweg und Sohn. 1905.

THERE is probably no chemist living who is better qualified to write upon modern developments in the theory of inorganic chemistry than Prof. Werner, and his book deserves the careful attention of all interested in the study of this subject. The book, which is one of a series of monographs on scientific and mathematical topics, gives a complete account of the views of the author and of other eminent chemists regarding the structure and spatial arrangement of the molecules of inorganic substances, and while the author aims at giving broad outlines rather than details, the treatment is, comparatively speaking, very full. The subject is divided into three sections. In the first of these is explained the modern development of the idea of an element and of the Periodic System, with special reference to Prof. Werner's own theory relating to this system. The second part deals shortly with compounds of the first order, and with the doctrine of valency, while the last section, which forms the greater part of the book, gives a complete *résumé* of compounds of higher order, and of the doctrine of co-ordination, in which region the author has done so much exceedingly valuable work.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY EXAMINATIONS.

To the Editor of the Chemical News.

SIR,—I note with pleasure the letter from your correspondent "One of Many" on the above subject (*CHEMICAL NEWS*, xcii., p. 200). His remarks about obtaining the F.I.C. by way of the B.Sc. are true and very appropriate.

As regards the excellent scheme he has outlined I have only one exception to make, namely, that in my opinion Stages III. and IV. (Mathematics) are going rather beyond the requirements of most technological chemists. Stage II. appears to me to be amply sufficient. In this connection I may say that even in the B.Sc. (London) Examination the syllabus is now so arranged that Mathematics in its higher stages is not so compulsory as formerly, and the subjects for the Inter. B.Sc. do not necessarily include Mathematics.

I would venture to suggest that in place of the higher Mathematics, Natural Sciences be substituted, since they are of importance and use to chemists. I refer more particularly to Heat and Light, Magnetism and Electricity, which are entirely omitted from your correspondent's scheme. It is only by the adoption of some such arrangement as proposed by "One of Many" that many technological chemists can obtain anything like a recognised "hall-mark" in their profession, and at the same time convert the, at present, almost valueless certificates into something of more generally recognised merit.

In conclusion, I trust that "One of Many" will take my criticism of his scheme in the right spirit. I can assure him that I am obliged for his taking up the subject in so able a manner.

Apologising for the trespass on your space, I am, &c.,
TECHNICUS.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 15, October 9, 1905.

Derivatives of Cyclohexane.—P. Freundler and E. Damond. — The authors prepare bromocyclohexane ($C_6H_{11}Br$) and iodocyclohexane ($C_6H_{11}I$). These derivatives do not condense easily with the sodium derivatives, on account of their tendency to decompose into cyclohexane and the hydricid. Only traces of the normal product of the reaction can be obtained by heating the chloride or iodide with sodium acetylacetic ether, either in presence of absolute alcohol at 100° in a sealed tube or in xylene solution at 150° . The former method gives slightly better results. In addition to these products, the following were also prepared: — Cyclohexylcyanacetic ether, $C_6H_{11} \cdot CH < \begin{smallmatrix} CN \\ CO_2C_2H_5 \end{smallmatrix}$; cyclohexylmalonic ether, $C_6H_{11} \cdot CH(CO_2C_2H_5)_2$; and cyclohexylacetic or hexahydrophenylacetic acid, $C_6H_{11} \cdot CH_2 \cdot CO_2H$. The ethylic ether prepared from absolute alcohol and hydrochloric acid gas is a liquid of pleasant smell which distils at $211-212^\circ$ at 766 m.m. pressure.

Decomposition of Meta- and Para-nitrobenzylic Alcohols under the Influence of Aqueous Soda and Alcoholic Soda.—P. Carré. — Meta- and para-nitrobenzylic ethers, in the same manner as the ortho-nitrobenzylic alcohol, when in alkaline solution show phenomena of oxidation and reduction depending on their nitro-grouping and their alcohol-grouping. The stability of these three nitrated alcohols towards alkalis increases from the ortho- to the meta-derivative. The decomposition of the ortho-alcohol is distinguished from that of the meta- and para-alcohols by its greater rapidity, and by the formation of substances which result from the facility of reaction of the groups situated in the ortho-position, whilst the meta- and para-alcohols give exclusively products which result from the oxidation of the alcohol group and from the reduction of the nitrated group. Ortho-nitrobenzylic alcohol can be further distinguished by the presence of amine substances in the products of decomposition, these latter not being formed in the case of the meta- and para-nitrated alcohols.

Certain Phenolic Ethers having a Pseudo-allylic Chain, $ArC(CH_3)=CH_2$.—MM. Béhal and Tiffeneau. — In a former research the authors discovered the conditions of preparation and the physical constants of certain aromatic pseudo-allyl derivatives. They now investigate the properties and reactions of these derivatives when subjected to hydrogenation, oxidation, and fixation of IOH.

No. 16, October 16, 1905.

Absolute Desiccation of Vegetable Substances.—L. Maquenne. — The author makes a series of experiments on the desiccation of vegetable matters, and finds that amyl bodies, and especially pure starch, can be easily and rapidly desiccated in dry air. Under these conditions the loss of water is greater than in a stove. The grains of starch also dry better in a vacuum at 40° than in air at 110° . The author formulates his conclusions as follows:—1. The constancy of weight of a vegetable product (probably also the majority of mineral and organic substances), after remaining some time in a stove in ordinary air, can at no temperature be considered as perfectly desiccated. 2. The use of an ordinary stove is absolutely useless for the rigorous analysis of very hygroscopic bodies such as starch. 3. The absolute desiccation of such substances can only be effected even at a high temperature in a medium absolutely free from water-vapour. It is apparently complete in one hour by

heating at 120° and two hours at 100° in a current of dry air. Under these circumstances the matter remains unchanged, and the proportion of water is found to be less by 1 per cent than that which is present after a much longer period of desiccation by the ordinary methods.

Basicity of Pyranic Oxygen. Halogen Combinations of Dinaphthopyryl with Metals and Metalloids.—R. Fosse and L. Lesage. — The radical dinaphthopyryl, $—CH < \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} O$, forms a large number of double salts with the halogens and mineral elements in the same manner as potassium. In the present paper the authors give the formulæ of new halogen double salts containing dinaphthopyryl and one of the elements, platinum, lead, iron, zinc, tin, bismuth, arsenic, and antimony,

MISCELLANEOUS.

Issue of Work of Art on Gunpowder.—Mr. Oscar Guttman, M.Inst.C.E., F.I.C., F.C.S., of 12, Mark Lane, London, E.C., intends to publish a facsimile reproduction of all ancient pictures and engravings dispersed in libraries all over the world, referring to the invention, early manufacture and examination, and first use of gunpowder. It is to be a work of art, printed by hand on the finest handmade paper, with an imitation fifteenth century binding, and limited to about 300 numbered copies. The publication is made in the interests of science, not only without profit, but by selling a number of copies for collectors at a higher price, the subscribers will get it under cost price. Scientific and industrial men who have not received a direct invitation should apply for particulars to Mr. Guttman.

The Milan International Exhibition, 1906.—Celebrating the opening of the Simplon Tunnel, the first International Exhibition held by the Kingdom of Italy will be opened at Milan on April 15th next. It will be under the high patronage of the reigning monarch and supported by a powerful British Commission, of which Mr. Arthur Serena has been appointed Honorary Executive Commissioner. The Commission also includes Lord Brassey, Sir Albert Rolitt, M.P., Sir William Holland, M.P., Comm. L. Allatini, Cav. P. Polenghi, and others, with as Joint Secretaries Mr. Kenric B. Murray (London Chamber of Commerce), Sir Edward Fithian (Associated Chambers of Commerce), and Sig. Tullio Sambucetti (Italian Chamber of Commerce). The British Government have voted the sum of £10,000 to the National Section. H.M. the King of Italy will offer prizes to the extent of £1600 to exhibitors. This amount will be divided as follows:—

1. A prize of £200 for automatic safety couplings for railway rolling stock.
2. A prize of £200 for the best method of testing high voltage electric currents without danger to the operator.
3. A prize of £400 for the best and most original exhibit of machinery or manufacturing process.
4. A prize of £200 for the best established method of distributing healthy and pure milk in centres of population.
5. A prize of £400 for the best type of popular dwelling adapted to the climate of northern Italy.
6. A prize of £200 for motor boats.

In addition to the foregoing there will be given a National Prize of £200 to the public institution or private society which, during the last ten years, has been most successful in the work of reclaiming waste lands in mountainous districts, and in the improvements of pasturage. The Exhibition will occupy close on 200 acres, of which the buildings will occupy 42. Among the other leading nations that will be officially represented are included France, Germany, Austria, the United States, &c. Of the ten sections the Exhibition will be divided into, only one, that

of Fine Art, is national. The others include Land, Sea, and River Transportation (Locomotives, Motors, Trams, Carriages, Ship Models, Shipping Equipment, Nautical Instruments, &c.), Aeronautics, Meteorology, Manufacturing and Decorative Arts, Machinery in Motion, Social Economy, Agriculture, Hygiene, Fisheries, &c. These special inducements to exhibiting will doubtless possess attraction for British manufacturers, inventors, and others, who should without loss of time address themselves for further particulars to the Hon. Executive Commissioner of the British Section, 1 and 2, Oxford Court, Cannon Street, London, E.C.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Institution, 5. General Monthly Meeting.
Society of Chemical Industry, 8. "Evaporation in vacuo of Solutions containing Solids," by J. Lewkowitsch.
FRIDAY, 10th.—Physical, 8. "The Question of Temperature and Efficiency of Thermal Radiation," by J. Swinburne.
"Note on Constant-deviation Prisms," by T. H. Blakeley.

ERRATA.—P. 175, col. 2, line 12 from top, for 21963'697 read 21963'258.
Line 30 from top, for 14'575 read 14'0575.

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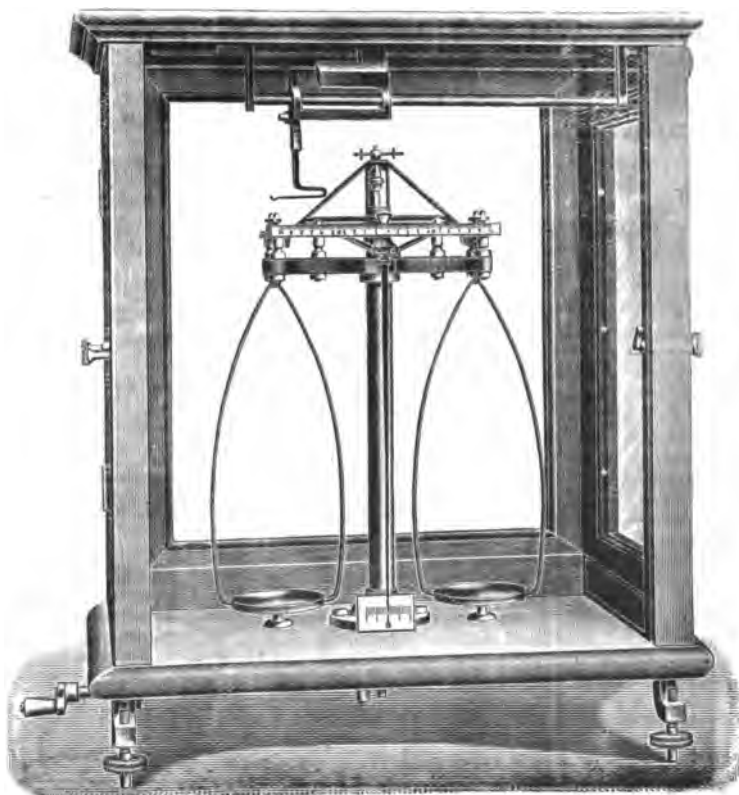
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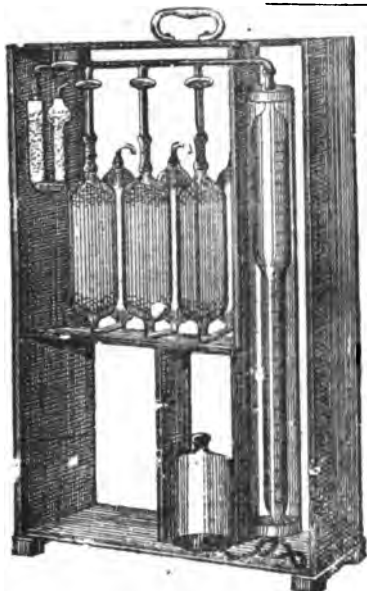
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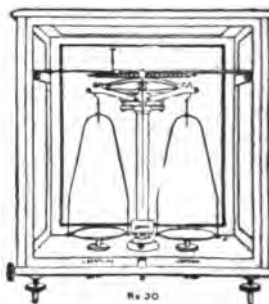
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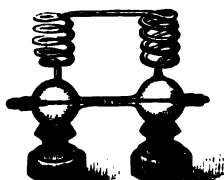
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THE CHEMICAL NEWS.

VOL. XCII., No. 2398.

ON A RADIO-ACTIVE SUBSTANCE DISCOVERED IN THE TRANSVAAL AND EXPERIMENTS CONNECTED THEREWITH.*

By R. LEWIS GOUSENS, M.Inst.E.E.

(Concluded from p. 206).

CHEMICAL experiments were then undertaken with a view, if possible of getting rid of the opaque matter, which, as stated before, appeared to be titanium. A small quantity of the zircon and rutile was smelted down, using carbonate of soda as a flux.

The residue was then treated with hydrochloric acid and put into solution. After standing for several hours a small amount of precipitate of a whitish colour was formed, which was increased by adding ammonium hydrate; this was filtered off, and the precipitate obtained I will refer to as No. 1.

Ammonium chloride was then added, and No. 2 precipitate of a reddish colour was brought down. The solution was again filtered off, and ammonium carbonate added, resulting in No. 3 precipitate of a light grey colour. Sodium phosphate was then added to the filtrate, in which, after standing for several days, no further precipitate was observable. The solution was then evaporated down, leaving behind the sodium and potassium carbonates, which I will allude to as precipitate No. 4.

Precipitate No. 2, of a reddish colour, showed the presence of ferric iron. Although the greater portion of this metal had been extracted by magnetic means (as before described) there are certain compounds of iron which are non-magnetic, which accounts for its existence in this precipitate. I found that—

- No. 1 Precipitate was slightly radio-active.
- No. 2 Precipitate was the most radio-active of the four precipitates.
- No. 3 Precipitate was non-radio-active.
- No. 4 Precipitate was strongly radio-active at first, the radio-activity then decaying to a point I would call fairly radio-active, it then remaining constant.

As precipitate No. 4 was apparently free from opaque matter, I tried its effect on a photographic plate; the experiment so far succeeded that a portion of the image of the object, which was a small brass wheel, was impressed thereon. The original quantity, however, of the concentrates treated was very small, viz., about 3 ounces, and, moreover, the object of the chemical experiment was not only to get rid of the opaque substance, but if possible also to bring down all the radio-active matter into one precipitate; in this I had not so far succeeded, because, as detailed above, the radio-active matter was distributed over three of the precipitates in varying quantity, the apparent reason for this being alluded to hereafter.

A larger quantity of the concentrates therefore was then treated, the method of procedure being slightly varied. After smelting down with carbonate of soda as a flux, and steeping the product in strong hydrochloric acid, which was boiled, distilled water was added; a fair amount of precipitate made its appearance containing silica with a small proportion of iron, which I shall allude to as precipitate A. This was extracted by filtration, and on adding ammonium hydrate and ammonium chloride to the filtrate, a further precipitate (B) was obtained. Precipitate C was obtained

by adding ammonium carbonate to this filtrate; the solution was filtered again, and on adding sodium phosphate no further precipitate was observable. The solution was then evaporated down, leaving behind carbonate of soda, &c., which I shall allude to as precipitate D.

Precipitate A was very slightly radio-active, less than No. 1 precipitate in the first experiment.

Precipitate B was more radio-active than any sample of concentrates or precipitates in my possession up to that time.

Precipitate C was non-radio-active.

Precipitate D was strongly radio-active at first, decaying in a similar manner to that of No. 4 to a point when it became constant.

This experiment was more successful than the previous one, as I had now obtained a greater proportion of the radio-active matter in the one, viz., precipitate B. Both precipitate 4 and precipitate D were at first very active, but the radio-activity (as stated above) decayed after a time to a point considerably below that of precipitate 2 and precipitate B, afterwards remaining constant.

That any radio-active matter should finally come down with the carbonate of soda was at first somewhat surprising, as precipitate 3 and precipitate C were absolutely non-radio-active.

I have come to the conclusion that this is due to the product of the emanation and not to any of the original radio-active matter, all the latter having, in my opinion, come down in the first two precipitates, principally in the latter of these two.

My reasons for coming to these conclusions are:—

1. That from experiments already made, the radio-active matter being combined with the titanium and iron (I believe the zircon when separated out will be found to be non-radio-active), has come down with these metals in precipitates A and B.

2. Precipitate C is non-radio-active.

3. That according to Professor Rutherford (I shall frequently quote this investigator as my authority in the argument), all the products of the radium emanation are soluble in strong acids and partly so in ammonia. In the publications of this *savant*, and those of other authorities, I can only find one method that has been adopted of precipitating these products, i.e., by evaporating down the solution in which they have been dissolved. It is only reasonable to suppose, therefore, that when hydrochloric acid was added to the concentrates which had been smelted down with carbonate of soda, that the products of the emanation remained in solution until the latter was finally evaporated down, leaving behind the said products with the carbonate of soda.

4. The character of the radio-activity of this residual product, viz., it was very active at first and then decayed down to a constant quantity. This is the character of the product of radium when it arrives at the state known as radium D, which rises again in activity several months afterwards, remaining in this state for about forty years.

I have lately tested this precipitate, which is about four months old, and find that its activity is rising again, so that it appears to correspond with the product known as radium D.

The corollary of the above statements also is that I believe the radio-active substance to be radium, not only for the reasons already given but also for the following:—

The final products of both thorium and actinium (the only two known elements in addition to radium from which an emanation is evolved) have been found, and are known as thorium C and actinium C. Both of these final products are rayless, i.e., give forth no radio-activity. Now sufficient time has by now elapsed for the product of the emanation from the radio-active matter in the concentrates to have reached the final product, assuming the same to be either actinium or thorium, and therefore in either case it should be non-radio-active. As, however, it is radio-active it cannot be derived from either thorium or actinium.

* A Paper read before the British Association (Section B), South Africa Meeting, 1905.

On the other hand, the final product of radium has not yet been found, and according to the time given by Professor Rutherford representing the periods necessary for the successive changes to take place, the product of the emanation from the radio-active matter in the concentrates should be in the state radium D if it is this element. Tests tend to prove that this is the case, as radium D is radio-active, giving out β -rays, and the radio-activity remains fairly constant over a considerable space of time.

Precipitates 4 and D are radio-active, and otherwise appear to coincide with the characteristics of the element radium D.

I may mention that the total period of time as given by Professor Rutherford necessary for 50 per cent of thorium products to be successively transformed from the emanation down to the final product thorium C is eleven hours, fifty-six minutes. Now supposing this period had not elapsed between the time when the carbonate of soda was brought down with the products of the radio-active matter and the time when the latter was tested for radio-activity, it is impossible to understand how it could have been derived from thorium, because with thorium the rate of decay of the activity of its products decreases in each period, according to a simple exponential law, with the time. Now the activity of radium products does not decay throughout the whole range of their successive changes in accordance with the above law, neither does the activity of precipitate 4 or precipitate D do so, and are therefore dissimilar to the results obtained with thorium products, and similar to those obtained with radium products.

Having obtained a precipitate, viz., B, that was more radio-active than any other sample in my possession, and which was kept in a tube before treating further by chemical means, some photographic experiments were tried. The precipitate was placed on a plate with two objects to be photographed, in a light-tight box. After about three days' exposure a good radiograph resulted, the edge of the mineral where heaped up on the plate being clearly defined all round with an impression of the objects.

Without replacing the precipitate in the tube the experiment was repeated, placing two sheets of brown paper between the mineral and the plate. No result followed, the reason being probably that between the two experiments the precipitate was exposed to the air, and the emanation allowed to escape. I accordingly replaced the precipitate within the tube, corked and sealed it, keeping it in this condition for over four days. At the end of this time the experiment was once again repeated, pouring the mineral out on black paper, the latter being on top of the plate within the light-tight box, and closing the covers of the latter as quickly as possible. The black paper referred to was that used for protection of sensitive plates, and is very opaque to the ordinary rays of light. On development distinct lines of light could be seen on the negative, proving that they had been produced by rays emitted from the precipitate. My reason for keeping the precipitate corked and sealed within a tube for over four days is that it takes about this period of time for a proportion of the emanation to be successively transformed down to radium D, the object being to obtain all three classes of rays, because, as stated before, radium itself, the emanation, and radium A only give out α -rays; radium B is rayless, and radium C gives out all three classes of rays, and radium D β -rays and probably γ -rays.

It is therefore these two latter products that are required to ensure good results in physical experiments, and it is clear that if the emanation is allowed to escape these products will not be obtained at all, as the emanation (if I may so use the expression) is the progenitor of them all.

Now, as mentioned above, although the α -rays are present when the concentrates are first extracted, this class of rays is not of great penetrative power; an aluminium plate of only 0.0005 centimetre thick is sufficient to decrease the intensity to one-half and a mica sheet 0.01 centimetre thick is sufficient to absorb all the α -rays.

Now, aluminium is not so opaque as most of the other metals, certainly nothing like so much as either iron or titanium; the latter metals being therefore combined with the radio-active matter in the concentrates absorb these α -rays, and in the majority of cases prevent the detection of their presence. Their effects can sometimes be made apparent, because if the concentrates, after being exposed to the air, are spread on a photographic plate, on developing the latter, two or three black spots can, as a rule, be seen, showing that there are a few light-giving particles in the mineral whose α -rays are not entirely cut off.

The question as to whether radio-active ore, as found *in situ*, is in the proper condition for obtaining good physical results here arises. From what has already been stated it is evident that this largely depends upon its porosity. Take, for example, pitchblende, the European ore in which radium is found; this would be classed in common language as a hard rock of close grain. Whatever emanation is therefore produced by any radium that may happen to be present would be occluded within the pores and interstices of the rock, and it would be here transformed continuously and successively into the various products, radium A, B, C, and so on. It must also be remembered that the uranium in pitchblende, before it reaches its final state which is rayless, is transformed into uranium X, which emits β -rays and γ -rays, whilst uranium itself gives out α -rays. There are therefore present all three classes of rays from this source alone, and ore of this character is therefore, with whatever radium its products and other radio-active substances that may happen to be present, in a condition which will produce good results from physical experiments.

On the other hand, taking the concentrates described in this paper as an example, and which, so far as I can discover, contain only one radio-active substance, i.e., radium, these are not in a condition for obtaining good results by physical means when first extracted. The ore where found *in situ* is of a porous character, the ilmenite and rutile in which the radio-active matter is combined being mechanically and somewhat loosely intermingled with silica. Whatever emanation is therefore produced by the radium filters through the silica, is dissipated in the air, and therefore a large proportion of the succeeding products from the emanation is lost.

It may be argued that a large proportion of these products should remain in the ore, as when the emanation filters through the silica a certain amount would cling to each particle, covering it with an invisible film of radio-active matter. This I venture to think is correct; but, on the other hand, most of this product would be washed away during the process of concentration.

Ore, therefore, of this character when extracted is not at first in a good condition for obtaining definite results by ordinary physical means, and it clearly follows that whereas one class of ore in the quantity of radium contained may be richer than another, the same may be poorer in the quantity of the products of radium than the other owing to its greater porosity. It is for the above reasons that it is necessary that the concentrates should be kept within a closed vessel after extraction for the purpose of obtaining results by ordinary physical means, and I opine it was owing to the lack of taking this precaution that other investigators to whom I sent samples failed to obtain results, which I would add, however, is altogether excusable, as the finding of radium under the conditions described is altogether a new occurrence.

The fact that the concentrates were placed in bottles when extracted was a fortuitous circumstance, and if this had not been done the discovery would probably not have been followed up or this paper written, as of course it was necessary to obtain confirmatory results by more means than one.

Having obtained, therefore, good results from precipitate B by photographic means, experiments were made with this and No. 2 precipitate for the purpose of extracting if possible the radio-active matter therefrom.

Finding that Professor Rutherford had extracted radium from thorium and actinium solutions by adding a soluble barium salt and then precipitating as sulphate, and that Madame Curie had stated that radium always follows this element in its reactions, I dissolved precipitate 2 in dilute sulphuric acid, and added barium nitrate which had been dissolved in distilled water. The barium was precipitated as sulphate, the solution was filtered off, and on testing the barium (precipitate 5) I found it to be highly radio-active, more so than the original precipitate 2.

I made several successive precipitations with barium, but found all these latter to be non-radio-active, all the radio-active matter having apparently combined with the barium in the first precipitate. The filtrate was then evaporated down, leaving behind a residue (precipitate 6) which was very slightly radio-active. This radio-activity is probably caused by the products of radium brought down in a similar manner to the quantity brought down with the carbonate of soda (precipitate 4 and precipitate D) in the original tests; the radio-activity was not so great as that of precipitate 4 or precipitate D, as it represents only that of the products formed during the time intervening between the first and second tests.

The quantity of matter as represented by precipitate 2 was small and the quantity of barium (precipitate 5) was not much smaller; the improved radio-activity therefore was brought about not so much by the reduction in bulk of the matrix of the radio-active matter, but by the fact that the opaqueness of barium is not so great as that of the original matrices of titanium and iron.

The fact that the radio-active matter combines so readily with barium is a proof (or at least an indirect one) that radium is present; it certainly is not thorium or actinium, as these elements do not chemically combine with barium.

Precipitate B was then treated in a similar manner, with the exception that I used hydrochloric acid instead of sulphuric; the barium (precipitate E) readily combined with the radio-active matter, and the solution was finally evaporated down, leaving behind precipitate F. The latter precipitate I found to be more radio-active than precipitate 6, resulting doubtless from the products of the emanation brought down from a larger quantity treated than in the previous test. Precipitate E was more radio-active than any sample obtained up to the present time, and it was placed in a corked tube and sealed.

An important point to note in connection with these experiments is that whilst barium will readily combine with the radium, it does not appear to do so with the products of the emanation; the latter come down with the final precipitates after the solution is evaporated, the activity of the same decaying in a similar manner to that of precipitates 4 and D. I have not attempted to separate the radio-active matter from the barium, as the total quantity brought down is somewhat small; in fact, it represents that extracted from only 1 lb. of concentrates. I shall endeavour to do so when the quantity brought down is greater from a larger quantity of the raw material.

The process of separating radium from barium by fractional crystallisation is somewhat lengthy and tedious, and therefore it cannot be stated that adding barium for the radio-active matter to combine with is the best method to be adopted when working on a large scale. Professor and Madame Curie were obliged to adopt this method, as barium already combined with radium exists in pitchblende, whereas in my case this substance was added, as none was found in the crude ore. If something else can be found which will combine with radium and be more easily extracted from it, it will be advantageous. If the method of adding barium has to be adopted, the whole process can be materially shortened by adding the barium nitrate solution instead of the ammonium hydrate to the original solution, and thus the radio-active matter can be immediately extracted with the barium.

Further experiments go to prove that the radio-active matter discovered is radium, as in addition to those already detailed in this paper, I have tried others with thorium,

euxenite, monazite, and other radio-active substances, and find that none, with the exception of radium, correspond with the results obtained; at the same time, until the radio-active matter has been actually extracted from the barium, I suppose I should not state finally that it is radium, as some of my hearers will probably think that the old adage "Seeing is believing" perhaps applies in this case.

The work so far completed may seem to have been somewhat arduous and lengthy, but it has been nothing compared to that of the pioneers in the investigation of radio-active substances. I allude, of course, to the work of Madame and Professor Curie, who, after overcoming great difficulties, brought forward to the view of a wondering world the element known as "Radium."

I should also add that since the first portion of this paper was written, results have been obtained by a metallurgist in Europe who thinks that from the small sample sent the same may be due to the presence of thoria. I, however, reiterate that I think it is due to the presence of radium, having regard also to the nature of the origin of the deposit which I shall now proceed to describe.

Some time after the discovery had been made of the radio-matter in the alluvium, I proceeded again to that part of the country for the express purpose of endeavouring to find out the source from which it was derived. After tracing the course of the alluvium for over 40 miles in length, it came to a sudden termination in a valley or kloof, surrounded on the three sides by kopjes of Waterberg sandstone, the source being what appears to be an extinct mud pipe or vent, similar in many respects, and dissimilar in others, to those that form the well-known diamond mines of South Africa.

The exact spot appears to be clearly defined, as although the usual trees of the bush veldt, consisting principally of the *Syringa* and *Boekenhout* type, grow in profusion along the slopes of the valley, at the point indicated there is a marked and an entire absence of these trees, shrubs, or grass. I attribute this to the fact that at the crater's mouth the soil consists nearly entirely of dry clay mud mixed with the concentrates before alluded to, whilst lower down on the alluvium there exists silica of coarser grain, which has evidently been derived from the Waterberg sandstone, through which the pipe has intruded, the latter being a better class of soil for the growth of vegetation and trees than the former.

The walls of the pipe cannot be seen, as they are hidden by the mud lava that has completely covered up its mouth. I, however, picked up in a water-course in the vicinity some samples of igneous rocks, from one of which a rock-slide has been made. Examination under the microscope (confirmed by Professor Young) proves it to be dolerite. Two of the other samples procured are hæmatite or specular iron.

These rocks are frequently met with in the vicinity of diamond mines in Griqualand West, and elsewhere; dolerite, somewhat altered and under this condition known as basalt, is usually found on the outer circumference of a diamond pipe in the form of more or less rounded boulders; hæmatite, or specular iron, is, as a rule, disintegrated and mixed with the alluvial soil, giving it its well-known red appearance.

Now, comparing the nature of the concentrates before alluded to with the deposit of a diamond mine, in both are found magnetite and ilmenite (or what the South African diggers usually call carbon); in some diamond mines zircon is also found, and rutile occasionally in small quantities.

The chief point of dissimilarity is the difference in the size of the grain of the constituent parts when comparing the deposit from both sources.

The largest size grain of any particles of the concentrates is not much bigger than from two to three times that of a pin's head, whilst individual pieces of mineral or pebbles from a diamond mine often attain a considerable size; garnets are sometimes found as large as an apple, ilmenite larger than walnuts, whilst even diamonds occasionally astound the world by their great size.

The other point of dissimilarity is the amount of overflow from this pipe, which extends, so far as length is concerned, for over 50 miles, and whilst this extent of overflow has been helped by a river in the neighbourhood depositing the alluvium, yet the amount of mud-lava gushing forth originally from the mouth of the crater must have been very great, as the alluvium with the radio-active matter in it extends on the one side of the river over the distance named without any large breaks, and, similarly, on the other side of the river for a distance of about 30 miles; the width and depth of the alluvium varies according to the contour of the ground (the latter being Waterberg sandstone) over which it has flowed and been deposited, being from a few feet up to 2000 feet in breadth and from a few feet up to 30 feet in thickness.

There are signs that this river, in consequence of carrying this alluvium and depositing it along its banks, has swerved in places from its original course; it is not practically carrying this alluvium now, as it does not run through the pipe, but (as stated before) in its neighbourhood, and therefore I do not find any radio-active mineral, beyond traces here and there, in its bed as it exists to-day; the presence of the latter commences some distance from the edges of its banks over the dimensions already given, so that the alluvium at present in the bed of the river is pure silica and iron oxide derived from the Waterberg sandstone.

The radio-active alluvium has been found by fire assay to contain traces of gold, but this has evidently been derived from the Waterberg sandstone over which it has flowed, as this metal has been proved to exist in this stratum in quantities from traces up to a half pennyweight to the ton.

Now, I do not know of any diamantiferous pipe that has overflowed to anything like this extent. The pipes forming the Kimberley group of mines have not done so at all. Some of those in the Orange River Colony have overflowed compared with the above to a slight extent, as what are called yellow leads containing diamonds have been found in the alluvial soil some distance away from the pipe, and which I believe in some instances have led to the discovery of the latter. The Premier Mine in the Transvaal has perhaps also overflowed to a slight extent, although I think the deposit found in the neighbourhood is perhaps more due to its having been carried there by a strong spring that rises in the mine and runs through a portion of it. The fact that diamonds have been and are now found for some distance along the banks of the Vaal River can hardly be quoted as an example of overflow from the pipe itself, as this river, if it does not to-day run through a diamantiferous pipe, probably did so originally by a course now dried out.

Great as has been the flow before alluded to, it is of course quite insignificant compared with the enormous flows of other igneous lava sheets existing in South Africa. I allude principally to the diabase sheets that cover up thousands of square miles of country, and which have hidden the blanket reefs in the Witwatersrand formation, both on the east and west extensions. None of the pipes or vents through which these enormous flows of lava have issued forth and spread over the strata beneath have yet been found. This, of course, is due to the fact that the same have intruded only through the strata laid in the earlier geological periods, and are therefore antecedent by several ages to those that form the diamond mines of South Africa, as well as the one referred to containing the radio-active lava; there is existing in places an enormous thickness of different strata overlying these diabase sheets, consisting of black reef formation, dolomite, the Pretoria series, Waterberg sandstone, Dwyka conglomerate, the Eccca shales of the Karroo series, and the coal measures, whilst the Kimberley group of mines has extended right up through the Eccca shales of the Karroo system.

These pipes or vents by which the diabase was brought up must be of a purely volcanic nature, but the question arises are diamantiferous pipes, or the one described in

this paper, volcanic or more thermal in their origin? Mr. Gardner Williams, the General Manager of De Beers Consolidated Mines, in his book entitled "The Diamond Mines of South Africa," has expressed the opinion that the pipes forming the diamond mines of South Africa were formed more by thermal than volcanic action. I am of opinion that at least this is so in the case under review, which means that the mud-lava has been brought up from unknown depths, accompanied by thermal waters, vapour, and steam, and has welled over the mouth of the pipe, the comparatively large quantity of alluvium being deposited in the manner before described.

It may be mentioned that the samples with which nearly all my experiments have been done came from a point on the alluvium over 40 miles away from the crater; whether the concentrates in the pipe will be richer in radio-active matter cannot as yet be positively asserted. A small surface sample in my possession does give rather better results. I would, however, here add that should the radio-active lava become more solid in its nature as depth is attained, i.e., more of the nature of blue ground, as found in a diamond pipe, following the line of reason as detailed before in this paper, it should be richer in the products of radium than the ore in the upper levels of the pipe or that comprising the alluvium. The question, however, will soon be decided, as I hope shortly to undertake exploratory work at the source itself.

Assuming that the radio-active matter discovered by radium, it is necessary to say something with regard to its life.

The life of radium, or perhaps I should say "the stability of its atom," has been computed by Professor Rutherford at eight hundred years, i.e., the time taken for radium to be half transformed, whilst its average life is taken at eleven hundred years. These figures have been arrived at by mathematical deduction from experiments made from concentrated radium; I should think, however, that from what has been stated previously, quoting Professor J. J. Thomson, that the life of radium when distributed throughout a mass of ore is somewhat longer than this. It will, however, serve my purpose to quote the above figures as being correct for the life of radium under this condition.

To account for the existence of radium as we now find it, Professor Rutherford has advanced the theory that it is being gradually produced from uranium, the only class of ore in Europe in which it has been found. Professor Ramsay has already practically proved that one of the products of the emanation from radium is helium, which appears in the earlier transformations, i.e., from the emanation to radium A and B; thus the one being a theory resulting from a mathematical deduction of the life of radium and the other a practical proof, are examples of the fulfilment of the dream of ancient philosophers who were constantly endeavouring to change one element into another.

Now, if radium is produced from uranium in European ores, whence comes the radium (assuming this to be the element) in the case under review? I have found no trace of uranium. On the other hand, it is practically certain that the mud lava, as now found *in situ*, was brought up and deposited more than eleven hundred years ago. We know that the Waterberg sandstone, upon which the alluvium rests, and which is a water-borne stratum, and although the most recently formed in the Transvaal (with the exception of the Lebombo Mountains on the border) was laid down more than eleven hundred years ago; in fact, this stratum belongs, in the opinion of geologists, if not to the archæan age, at least to the primary age, as no fossils exist therein. We are also fairly certain that the volcanic or thermal activity of that portion of the earth's crust known as South Africa occurred more than eleven hundred years ago. It is true that the Kimberley group of pipes has intruded into strata (viz., Dwyka conglomerate and Eccca shales, belonging to the Karroo system) of a younger age than the Waterberg sandstone, but in these

also no trace of fossils are found, and are therefore of great age.

It may be an open question whether the igneous rocks forming the pipes referred to were intruded into these various strata before or after the coal measures were laid down. No case exists to my knowledge where one has been intruded into the coal measures, and if a pipe were found under these strata it would the more certainly prove the point; however, it is the opinion of Transvaal geologists that the later volcanic or thermal activity in this part of the world certainly occurred more than 1100 years ago. Whence then is the radium derived, how is it being formed to-day, and when its life of 1100 years is completed what is the final product? To the latter portion of this question I believe no one can with certainty reply, because, as before stated, the final product has yet to be found. With regard to the former portion of the question, as one who is only commencing the study of the subject of radio-activity, I tentatively put forward the suggestion with all diffidence that the radium is being produced from titanium, and that in this case this element has taken the place of uranium in the European ores.

Two objections immediately present themselves to this theory. The first is that the metals in uranium, with which radium is combined, have all been found to be of high atomic weight, and it has been inferred by Professor Rutherford and others that there is some relation between this fact and that some of them are radio-active. The atomic weight of radium is 223.3, of barium is 136.4, of uranium is 236.7; whilst the atomic weight of titanium is very low (viz., 47.7), that of zirconium is somewhat higher, being 89.9.

Is it possible that a gap now exists in the sequence of the order of the elements, and that in ages long since gone by there were present a series of these elements whose atomic weights ranged from titanium on the one side in ascending order, and that these elements have been transformed successively from one to the other until, at the present time, that known as radium is the existing product?

This idea is suggested as it apparently coincides with that occupying the minds of all the leading scientific investigators, physicists, and savants of the world.

Sir William Crookes, in his paper entitled "Modern Views on Matter: The Realisation of a Dream," states that "men who devote themselves to science to-day have gone so far as to admit the possibility of resolving the chemical elements into simpler forms of matter, or even of refining them altogether away into ethereal vibrations of electrical energy."

This, in other words, means that everything in Nature is undergoing a change, and that radio-activity is going on all around us, but that in the majority of cases the change is so slow that our senses are not keen enough to perceive it nor our instruments sensitive enough to detect it.

The second objection to this theory is that if radium can be produced from titanium in the one case, why cannot it be in another? Why, for instance, cannot it be produced from the ilmenite (a compound of iron and titanium) which practically exists in varying quantities in every diamond pipe?

I have tested the deposit from several diamond pipes and found no radio-activity contained therein.

A somewhat analogous case perhaps may be cited in that of polonium, which is found in pitchblende. Polonium is radio-active bismuth, and is not so merely by induction from uranium or radium, but is of itself radio-active, and although it gives off no emanation, I have found that it is capable of exciting radio-activity in surrounding objects, thus proving (as stated in the earlier portion of this paper) that this induced radio-activity is not caused only by the emanation (as there is none in this case), but also must be produced by one or more classes of rays that are emitted by the substance itself. Now the ordinary bismuth of commerce is not radio-active, why, then, should the bismuth that is found in pitchblende be radio-active? Is some of the uranium in this case being transformed into

polonium in a similar manner to other portions which are being transformed into radium, and, if so, whence comes the original activity of uranium, i.e., from what element is this being derived?

To these queries and the objections I have raised to the theory that radium is being derived from titanium, I am afraid at the present time I cannot adequately reply, nor can I give any alternative theory. The whole subject of radio-activity has recently been likened by one professor to "a mountain whose peak is hidden in the clouds of heaven, and on whose slopes men still are struggling." I have been struggling on one of the lowermost slopes, but I trust by the time this investigation is completed to have risen to a higher level.

We have, however, the advantage to-day of having amongst us some of those great scientific investigators who have made the subject of radio-activity a special study, and who (to use the simile I have just referred to) are rapidly rising towards the peak of the mountain, even if they have not already gained the summit; their remarks, therefore, on some of the points brought forward will be deeply interesting.

TRIBO-LUMINESCENCE IN THE ACRIDINE SERIES.

By GILBERT T. MORGAN.

$\beta\beta$ -DINAPHTHACRIDINE, $C_{10}H_6$  $C_{10}H_6$, which was

first discovered by Reed (*Journ. Prakt. Chem.*, 1886, xxxv., 314), and subsequently re-examined by the author of this note (*Trans. Chem. Soc.*, 1898, lxxiii., 549), usually crystallises from alcohol in straw-coloured needles, but when allowed to separate very slowly from its solutions in alcohol, ethyl acetate, acetone, or benzene, it is deposited in transparent amber-coloured prisms, which become opaque when heated at about 120° and melt at 216°, having the same melting-point as the acicular crystals. Both forms of the base, when crushed between two ground-glass covers such as are used in closing gas-jars, emit a vivid yellowish luminescence; the phenomenon continues until the crystals are completely pulverised, and is accordingly more marked in the case of the hard prismatic variety. When the amber-coloured prisms adhere to the sides of the crystallising vessel the luminescence is observed on scraping the crystals with a spatula. This case of tribo-luminescence is of especial interest as being noticed in the case of a coloured substance which in solution also exhibits an intense bluish purple fluorescence.

Tribo-luminescence is not manifested by the yellow hydrochloride, hydriodide, methiodide, and ethiodide of $\beta\beta$ -dinaphthacridine, and the simplest base of the series—namely, acridine itself—does not exhibit this property when scratched or pulverised in the manner indicated.

Royal Institution.—A Christmas Course of Lectures (adapted to a Juvenile Auditory) will be delivered at the Royal Institution by Professor Herbert Hall Turner, D.Sc., F.R.S., on "Astronomy." The dates of the Lectures are December 28, 30, 1895, January 2, 4, 6, 9, 1906, at Three o'clock.

Awards at the Liège International Exhibition.—The international jury of the Liège Exhibition have conferred upon Burroughs, Wellcome, and Co. six Grand Prizes, three Diplomas of Honour, and three Gold Medals for the scientific excellence of their products, including "Wellcome" Brand Chemicals, "Tabloid" and "Soloid" Brand Products, "Kepler" Preparations, "Tabloid" Brand Photographic Chemicals, "Hazeline" Preparations, Pleated Compressed Surgical Dressings, "Tabloid" Brand Medical Equipments, &c.

THE INFLUENCE OF PHASE CHANGES ON THE TENACITY OF DUCTILE METALS AT THE ORDINARY TEMPERATURE AND AT THE BOILING-POINT OF LIQUID AIR.*

By G. T. BEILBY and H. N. BEILBY, B.Sc.

THE observations recorded in this paper are intended to prepare the way for a more direct attack on the problems of molecular cohesion by the establishment of clearer views as to the influence of changes of phase on the tenacity of ductile metals at various temperatures.

According to the phase theory of the hard and soft states in metals which was first developed by one of us more than a year ago, the changes of state from hard to soft and from soft to hard were shown to be due to the changes of phase brought about, in the one case by heat, and in the other by mechanical deformation or flow. In the ductile metals the crystalline is the mechanically unstable phase, while the amorphous only becomes thermally unstable when a definite temperature is reached.

The comparative mechanical instability of the two phases is well illustrated in the stretching of wires under tension. Annealed wires, which are in the C phase, stretch when they are stressed beyond the yield point; hardened wires, which are partly in the A phase, do not stretch—they break without extension when their limit of tenacity is reached.

The homogeneous C phase in ductile metals has no true breaking-point—it yields and stretches when stressed beyond the elastic limit, and in so doing it passes partly into the A phase, and rupture occurs at the breaking point of the mixed structure. The tenacity of the mixed structure approaches, but never quite reaches, that of the homogeneous A phase. For the purpose we had in view it was necessary to obtain the metals as nearly as possible in this homogeneous condition.

Wire drawing was the means employed for the breaking down of the C phase. After a wire had been stretched to four or five times its original length by drawing it through the holes of a wire plate, all the ordinary traces of crystalline structure disappear, but it still consists of minute granules of the C phase embedded in a matrix of the A phase. Further drawing at the same temperature alters the mixed structure only slightly; for each temperature there appears to be a certain mechanical equilibrium between the phases. By lowering the temperature of drawing, the C phase is further broken down into still smaller granules, and the mixture approaches more nearly to the homogeneous A state.

Our observations were made on wires which had been as completely as possible converted into the A phase by wire drawing at the ordinary temperature, and in every case the tenacity observed was higher than any which has been recorded by previous observers for equally pure metals.

Gold (Purity, 9997 per 10,000).

Tenacity at 288° abs. (15° C.) . . 15.6 tons per sq. inch.
" 53° " (-180° C.) . 22.4 " "

Silver (Purity, 10,000 per 10,000).

Tenacity at 288° abs. (15° C.) . . 25.7 tons per sq. inch.
" 53° " (-180° C.) . 34.4 " "

Copper (Conductivity, 100 per cent).

Tenacity at 288° abs. (15° C.) . . 28.4 tons per sq. inch.
" 53° " (-180° C.) . 36.0 " "

The wires broken at the ordinary temperature showed no general stretching. There was a slight extension of from $\frac{1}{4}$ to 1 per cent, due entirely to a sharp reduction of diameter at the actual point of rupture. At the boiling-point of liquid air all the wires stretched from 11 to 12 per

cent. This stretching was uniform over the whole length between the grips. This was confirmed by exact measurements of the diameter at a number of points.

The appearance of the fractured ends reveals several points of interest. In every case the copper wires showed the cupped formation at the extreme end. This formation is evidently due to the lower tenacity of the central core, due to the presence of gas bubbles which have been drawn out into long tubes or cells. The silver wires occasionally showed a slight cupped formation, but in this case the gas bubbles to which it was due were globular, as if they had been evolved at the moment of fracture. The gold wires were practically free from sponginess, and the fractures were almost perfectly viscous.

By drawing wires at the lowest possible temperatures we hope to obtain the ductile metals in their condition of maximum tenacity, and from the figures then available to be able to calculate the molecular cohesion at the absolute zero.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

THE starting-out material in this study was columbite from Lawrence County, South Dakota. Its specific gravity equalled 5.86. It contained 81 per cent of the mixed oxides of columbium and tantalum. The total quantity of substance decomposed by fusion with acid potassium sulphate (58.5 kilograms.) was 21.3 kilograms. Each fusion was made in a platinum dish, using 100 grms. of mineral and 275 grms. of acid potassium sulphate. While still liquid the mass was poured into a porcelain dish. When cold the fusion separated readily from the dish, and was broken into small pieces, which were boiled with water in large No. 11 evaporating dishes until thoroughly disintegrated; when they were transferred to precipitating jars, and the hydrates washed by decantation until the wash-water gave no precipitate or only a slight precipitate with ammonium hydroxide. The solution and the washings were evaporated to dryness. The residue was designated Part I. The moist hydrates of columbium and tantalum were covered with ammonium sulphide, and allowed to stand for several days. This ammonium sulphide solution was decanted and designated Part II. The remaining oxides were finally treated with very dilute sulphuric acid, and then thoroughly washed with water. The washings and the diluted sulphuric acid solution were also evaporated to dryness, and marked Part III. The residue labelled Part I. contained potassium and the bases from the mineral in the form of sulphates. It was dissolved in water, poured into five-gallon jars, and there precipitated with a slight excess of ammonium hydroxide. Having decanted the supernatant liquid the precipitate was washed once with water, after which the hydrates were covered with a solution of ammonium carbonate, and allowed to stand for several days. The ammonium carbonate solution was then syphoned off, acidulated with dilute hydrochloric acid, and any metal present precipitated with a slight excess of ammonium hydroxide. The hydrate obtained in this way was dissolved in dilute hydrochloric acid, and an excess of ammonium carbonate, together with ammonium sulphide, added to its solution. The iron separated in the form of sulphide, and with it there was a small amount of titanium. The filtrate from this precipitate was boiled with hydrochloric acid, and ammonium hydroxide added. The hydrate which was precipitated was ignited and tested as to its photographic power. It gave a picture after an exposure of five days. It contained uranium. It showed the greenish colour characteristic of U_3O_8 . After this it was fused with acid potassium sulphate, taken up in water, and the solution boiled. A precipitate formed on cooling,

* Read before the British Association (Section B), South Africa Meeting, 1905.

* *Proceedings of the American Philosophical Society*, 1905, xlv., p. 177.

but disappeared on warming, thus indicating the presence of members of the cerium group or of zirconium. On the addition of ammonium hydrate there separated a hydrate which, after filtration and washing, dissolved completely in a solution of oxalic acid. This pointed to the presence of zirconium. The hydrates were again precipitated, dissolved in sulphuric acid, and the solution neutralised with potassium carbonate, and saturated in the cold with potassium sulphate. By this precipitation the zirconium was obtained in the form of insoluble double sulphate, while the uranium remained in solution. After filtering out the zirconium potassium sulphate it was dissolved in hydrochloric acid, and zirconium hydrate precipitated with ammonium hydroxide. It was well washed with water, and dissolved in hydrofluoric acid. An equivalent amount of potassium carbonate was added, and, on evaporation, potassium zirconium fluoride crystallised out. Three grms. of this salt were obtained.

Analysis.—0.5043 gm. of the salt ignited with sulphuric acid gave 0.5272 gm. of $K_2SO_4 + ZrO_2$, and contained 0.2212 gm. of ZrO_2 , leaving 0.3060 gm. of K_2SO_4 .

	Calculated, K_2ZrF_6 .	Found.
2KF	41.05	40.47
ZrF ₄	58.95	59.52
	100.00	99.99

The uranium in the filtrate from the zirconium was precipitated with ammonium hydroxide, dissolved in hydrochloric acid, and an excess of sodium hydroxide added to this to obtain the glucinum. This was not found. The uranium was changed to nitrate, and the solution allowed to evaporate, when large characteristic crystals of uranium nitrate separated. The solution decanted from the original ammonium hydroxide precipitate, which contained manganese and allied elements, was treated with an excess of sodium carbonate. The precipitate produced was allowed to settle, the supernatant liquid decanted into other jars, and hydrogen sulphide passed through it. A small amount of a black sulphide was obtained. It consisted of zinc, iron, copper, and nickel (from the crucible tongs). The precipitate produced by sodium carbonate contained manganese, zinc, and iron. Ten grms. of it were dissolved in hydrochloric acid, and the iron removed by the basic acetate method. The zinc was then precipitated as sulphide. The latter was changed to chloride, and tested for gallium. Not a trace of the latter was found. Zinc lines alone were shown in the spectrum.

Tin and tungsten were contained in Part II. Part III. was not further examined. It may be concluded therefore that the columbite from South Dakota contains as acids—tantalum, columbium, titanium, silicon, zirconium, tin, and tungsten; as bases—iron, manganese, zinc, uranium, copper (?), and nickel (?).

The moist metallic acids, after having been washed with dilute sulphuric acid, were brought into a large platinum dish, and dissolved in fairly concentrated hydrofluoric acid. This solution was then filtered, through a hot water funnel, from undecomposed mineral, and from potassium silicofluoride (due to the presence of some potassium sulphate in the moist oxides). The hydrofluoric acid solutions were collected in large rubber dishes, and sufficient potassium hydroxide was introduced to convert the tantalum into potassium tantalum fluoride, most of which separated out and was removed by filtration. This precipitate was dried as far as possible by suction. It was washed once, and then allowed to dry in the air. It weighed 11 kilograms. The mother-liquor from the potassium tantalum fluoride was evaporated in stages, potassium hydrate being added. The columbium separated usually in hexagonal, hard, short crystals, such as separate from a strongly acid solution containing an insufficient amount of potassium fluoride. The total residue obtained in this way amounted to about 8 to 10 kilograms. These residues were decomposed by treating them with twice their own

weight of sulphuric acid, heating gently until the bulk of the hydrofluoric acid was expelled, and then evaporating until the mass fumed strongly, and maintaining the temperature until the excess of sulphuric acid had been almost completely driven out. Several hours were required for this. It is necessary in order to get rid of the hydrofluoric acid. The residual mass was boiled with water to extract the bases which dissolved as sulphates. The insoluble hydroxides were thoroughly washed and dissolved in hydrofluoric acid. The first crop of crystals, obtained by evaporation with potassium hydroxide, was removed, and the mother-liquor then evaporated to dryness with sufficient potassium hydroxide to change all of the metallic acids into double fluorides. A portion of these crystals (first crop) was dissolved in water, and the tantalum removed by adding dilute potassium hydroxide to the solution, which, after the formation of a permanent precipitate, was boiled for some time. The precipitate consisted mainly of potassium tantalum oxyfluoride. It was filtered out, and the filtrate evaporated to dryness. The residue was baked for some time at 200°. By this procedure some hydrofluoric acid was expelled, and, on taking up the residue with water and boiling, more potassium tantalum oxyfluoride separated. By repetition of this process all of the tantalum was removed from the solution. The only test relied upon for the detection of tantalum was the solution of this precipitate in a drop of hydrofluoric acid and evaporation to crystallisation. If needles separated their solubility in water was used to ascertain whether they were potassium tantalum fluoride or potassium columbium oxyfluoride. It is true that this test consumes considerable time, yet it is the only satisfactory means of determining with which of the metals the chemist is dealing. The formation of a precipitate by protracted boiling of a dilute solution of potassium tantalum fluoride is not conclusive, for Krüss and Nilson (*Ber.*, 1881, 1676) have shown that potassium columbium oxyfluoride deposits under like conditions a small amount of a salt containing less fluorine. Further, the double fluoride must be re-crystallised several times, so that it will be sufficiently free from acid that tantalum, if it is present in small amounts, may be precipitated by boiling.

Having freed the double fluoride from tantalum, it was dissolved in water and hydrogen sulphide conducted through its solution. A slight precipitate of platinum sulphide was obtained. The filtrate from it was evaporated to dryness and the residue baked. On dissolving in water more platinum sulphide was found, but when hydrogen sulphide was conducted through the filtrate no further precipitation took place. The first crop of crystals got by the evaporation of this solution showed the usual form of potassium columbium oxyfluoride. They were allowed to dry in the air and labelled crystals No. 1 (A). The filtrate from them was reduced to a small bulk. Strong hydrofluoric acid was added when the needles of potassium columbium fluoride (K_2Cbf_7) separated. These were dried between bibulous paper and labelled crystals No. 2 (B). Samples from these two crops of crystals were analysed.

Analysis of No. 1 (A).

0.53 gm. of salt gave 0.2346 gm. of oxide and 0.3161 gm. of potassium sulphate.

0.2346 : 0.3161 :: x/2 : 174 $x = R_2O_5 = 258.2$.

	Calculated, $K_2Cbf_7H_2O$.	Found.
K_2SO_4	57.81	59.64
Oxide	44.52	44.26

The crucible in which the ignition of oxide occurred was stained. This was undoubtedly due to the presence of tin, which had not been removed, although hydrogen sulphide had been conducted through the solution of the double fluoride.

Analysis of No. 2 (B).

0.8428 gm. of salt gave 0.3635 gm. of oxide and 0.4803 gm. of potassium sulphate.

0.4811 grm. of salt gave 0.2082 grm. of oxide and 0.2775 grm. of potassium sulphate.

0.3635 : 0.4803 :: $x/2$: 174 $x = 263.4$.
0.2082 : 0.2775 :: $x/2$: 174 $x = 250.1$.

	Calculated, $K_2C_2O_7$.	Found.	Found.
K_2SO_4	57.05	56.99	57.68
Oxide	43.93	43.13	43.28

Specific gravity of oxide (B) :—

18.5924 pycnometer + water, $t = 18^\circ$

0.2346 grm. of oxide taken

18.8270

18.7760 pycnometer + water + oxide 0.2346

0.0510 grm. water displaced 0.0510 4.60 sp. gr.

To determine the titanium content of the columbium oxide recourse was had to a comparison of the colour tint produced by hydrogen peroxide in an oxalate solution against known amounts of titanium hydrate dissolved in oxalic acid. Thus, 0.2262 grm. of columbium oxide was fused with acid potassium sulphate and the fusion dissolved in oxalic acid and diluted to 50 c.c. It gave a colour equivalent to 0.4 c.c. of the standard titanium solution (1 c.c. contained 0.00106 grm. of titanium dioxide). In other words, by this test the columbium oxide was thought to contain 0.000424 grm. of titanium dioxide, or 0.18 per cent.

Solubility of Crystals A.

One part of the salt was found to be soluble in a little over twelve parts of water. This is the solubility of potassium-columbium oxyfluoride.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 27th, 1905.

Prof. J. H. POYNING, F.R.S., President, in the Chair.

A PAPER ON "The Theory of Phasemeters" was read by Dr. W. E. SUMPNER.

Phasemeters are instruments of the dynamometer type for indicating the phase relations of the currents and potentials in alternating-current circuits. With few exceptions, they are made for use on multiphase circuits. Such instruments consist essentially of two sets of coils, of which one set is fixed, and the other forms a single moving system which is not provided with any form of control. The currents in one set of coils are determined by the voltages of the main circuits; while those in the other set are produced by the circuit currents. With rare exceptions the magnetic circuits of phasemeters are air-circuits, containing no iron, so that the magnetic fields associated with them are weak, and the instruments in consequence are of somewhat delicate construction. There, however, appears to be no reason why the use of iron should be avoided in these instruments, and the author shows in the paper that the theory of the instruments is the same whether they contain iron or not, and however the coils may be arranged; that they can be calibrated by direct current methods, although for use on alternating current circuits; and that a new type of instrument, containing iron, conforms to the theory given. In all the cases considered, it is assumed (1) that the induction density at any point due

to the current A in a fixed coil is represented by AF , where A is the instantaneous value of the current A, and F is a quantity dependent merely on the coil and the position of the point considered; and (2) that the principle of superposition holds, viz., $B = A_1F_1 + A_2F_2 + A_3F_3$, where A_1, A_2, A_3 are the currents in the three fixed coils, and the quantities F are functions of the position of the point corresponding to these fixed coils. The author shows that these assumptions hold good even when the path of the lines of force lies partly through (suitably laminated) iron and it is necessary to consider the effect of varying permeability and hysteresis. The main results of the investigation are :—

1. Phasemeters for multi-phase circuits are all equally accurate on balanced loads provided they have been correctly calibrated and possess no faults due to purely mechanical causes. Their accuracy is not affected by variations in wave-form or in current-frequency. The calibration of the scale is affected by the number of coils used in the instrument, by the ratios of the ampere-turns used with these coils, by the distribution of the windings, and by the magnetic nature and properties of the magnetic circuits, especially if these contain iron; but the accuracy of the indications is not dependent upon any of these considerations, if the working of the instrument is satisfactory from a mechanical point of view.

2. Phasemeters can be simply and accurately calibrated for balanced loads by means of a direct-current method of test.

3. The error of phasemeters on unbalanced circuits is generally serious for loads which are badly out of balance. The error, like that of a wattmeter, increases rapidly as the power-factor of the load diminishes. It can only be reduced at the expense of complication in the instrument, by increasing the number of coils used in the fixed and moving systems, and by arranging the coils and magnetic circuits to be symmetrical in regard to one another. If the true power-factor of the load is $\cos \phi$, the reading of the instrument is—

$$\cos \phi + \theta \sin \phi,$$

where θ is the phase error due to the unbalanced load, and is the product of two factors, one of which is the maximum value of θ determined by the amount the load is out of balance, and the other may have any value between +1 and -1 and determines whether the instrument reads high or low.

The Secretary read a letter from Mr. A. RUSSELL referring to one of the fundamental assumptions made by Dr. Sumpner. The magnetic force B, at any point on the conductor of the moving coil had been represented by $A_1F_1 + A_2F_2 + A_3F_3$, where F_1, F_2 , and F_3 were considered constant. The instantaneous value of the magnetic force at any point was the resultant of the three magnetic forces k_1A_1, k_2A_2 , and k_3A_3 , acting in fixed directions at that point. At any instant therefore—

$$B = k_1A_1 \cos \phi_1 + k_2A_2 \cos \phi_2 + k_3A_3 \cos \phi_3,$$

where ϕ_1, ϕ_2 , and ϕ_3 are the angles between B and k_1A_1, k_2A_2 , and k_3A_3 . As A_1, A_2 , and A_3 are not in phase with one another, the direction of the resultant magnetic force is continually altering, and thus ϕ_1, ϕ_2 , and ϕ_3 are functions of the time. Hence, also, the author's factors F_1, F_2 , and F_3 are not constants, but functions of the time, and thus the conclusions arrived at in the paper must be modified. Dr. Sumpner's method of calibrating by means of direct currents was novel and valuable, but little confidence could be placed in the readings of phasemeters when the applied waves of potential difference did not follow the harmonic law.

Mr. A. CAMPBELL, referring to the stepped nature of one of the calibration curves obtained by the author, asked if the use of a smooth core instead of a channelled one would result in a smoother curve.

Mr. K. EDGECUMBE expressed his interest in the paper, and said it was valuable because phasemeters were coming

* Probably too high because it was not heated enough to expel all of the sulphuric acid.

into general use, and the literature on the subject was small. Dr. Sumpner had stated in his paper that previous theories had neglected the question of the currents being unbalanced, but he pointed out that Punga in 1902 had described power-factor indicators, and showed how they could be used with unbalanced loads. It was important to define exactly what is meant by average power-factor. The author had given a mathematical definition, but a simpler definition would be that the average power-factor is that quantity which multiplied by the phase-voltage and the sum of the three currents gives the total power supplied to the line. A disadvantage of power-factor indicators was the difficulty of testing them.

Mr. W. DUDDALL asked if the author had assumed that the three voltages were in symmetrical phase relation, and pointed out that in practice differences of as much as 10° might occur.

Dr. SUMPNER, in reply, said that in the proof of the paper B was not the *maximum* flux but the effective part of it, that at right angles to the direction of motion of the conductor. He was aware that it was possible to obtain smoother curves, and had partially done it by a suitable distribution of winding giving a gradually varying flux. In reply to Mr. Duddell, he said he had assumed equal voltages and equal phase relations.

Prof. H. L. CALLENDAR described an Apparatus designed for Measuring the Coronal Radiation during an Eclipse.

The coronal radiation was received by a mirror with an aperture of 20 inches and a focal length of 45 inches, giving an image of the sun approximately 1 c.m. in diameter. The instrument was mounted equatorially, and was provided with a diagonal flat which projected the image to the side of the tube in a convenient position for observation with an eyepiece or a sensitive bolometer or thermopile. The tube of the telescope was fitted with a diaphragm of 15 inches diameter, which limited the aperture considerably but improved the definition. With this reduction, after allowing for obstruction by the flat, and for loss at the two reflections, the effective concentration of the rays at the focus was upwards of 1000 times. The absolute recording bolometer was designed for the determination of solar radiation in absolute measure by the electric compensation method. The radiation admitted through a measured aperture of 3 sq. c.m. was received on a blackened grid of fine platinum strips arranged in such a way as to intercept the whole of the admitted radiation. The increase of resistance of the grid was automatically recorded by means of a Callendar recorder of the usual pattern. The intensity in absolute measure was determined by observing the value of the electric current required to produce the same rise of temperature in the grid as the radiation to be measured. The apparatus was mounted on the tube of the 20 in. reflector, and the openings in the roof of the hut were arranged to permit of continuous records being taken between the hours of 10 A.M. and 3 P.M., so as to include the whole duration of the eclipse. Apart from its use for recording the variations of solar radiation, the instrument was intended for reducing to absolute measure the readings of the coronal thermopile. The coronal thermopile designed for the 20 in. reflector had a receiving surface consisting of ten small rectangles of very thin copper arranged in the circumference of a circle nearly fitting the image of the sun, so as to receive the greater part of the radiation of the inner corona. The copper rectangles formed the inner junctions of a series of thin bars of antimony and bismuth alloys arranged radially on a very thin supporting disc of mica. The outer ends of the couples were connected by thin copper strips at the outer circumference of the mica disc. The pile was constructed in two halves of five couples each on opposite sides of the disc, and the two halves were connected either in series or opposition through a suitable switch to the galvanometer. The mica disc carrying the thermopile was suspended in an ebonite ring by means of four thin connecting wires

attached to terminals fixed in the ring. The ebonite ring carried on one side a tube sliding in the eyepiece fitting by which the plane of the thermopile could be adjusted to coincide with the focal plane of the mirror, and on the other side a thick metal tube with diaphragms to screen the thermopile from draughts and from extraneous radiation. The galvanometer employed was of the movable-coil type, with a plane mirror 1 inch in diameter reflecting the image of a transparent millimetre-scale at a distance of 3 metres into a telescope of 2 in. aperture and 3 ft. focal length. The suspension was of very fine phosphor-bronze, giving a deflection of 5 c.m. for one microvolt with the thermocouple in circuit. In taking observations with the thermopile, it was possible either (1) to read the deflection of the galvanometer, or (2) to compensate the galvanometer deflection by introducing an opposing E.M.F. of known value into the circuit. A preliminary test of the apparatus with the thermopile directly exposed to radiation of known intensity, showed a deflection of nearly 25 c.m. for one-thousandth of a calorie per sq. c.m. per min., so that radiation one-millionth of full sunshine could be detected with certainty without using a mirror. When placed in the focus of the telescope, radiation one-thousand times smaller than this could be observed, so that even if the intrinsic heat-radiating power of the corona were only one ten-millionth of the solar surface it could still be measured to within 1 per cent. The essential point in the observations was to eliminate the variable effects of atmospheric radiation, for which a differential method of observation with the two halves of the pile was particularly suitable. In taking observations on the corona, the motion of the moon during totality was made use of to define the exact area of the corona corresponding to the differential reading. At the commencement of totality, the thermopile being centred on the sun, the inner corona on the eastern limb would be fully exposed, while on the western it would be partly covered by the moon. At the end of totality the reverse would be the case. The difference of the readings would correspond to the radiation of the strip of the inner corona uncovered by the motion of the moon between the two readings. The area of the strip of corona considered could be accurately determined from the times at which the readings were taken.

Mr. SLATER asked if, in the method employed by Prof. Callendar for getting rid of atmospheric radiation, he had assumed that the corona was symmetrical and that there were no prominences.

Prof. CALLENDAR said he did not think it was possible to distinguish between the radiation from the corona and that from prominences. The method he had employed did not depend upon the symmetry of the corona.

NOTICES OF BOOKS.

Select Methods in Chemical Analysis. By Sir WILLIAM CROOKES, Hon. D.Sc. (Oxford and Dublin), F.R.S., P.P.C.S., P.P.Inst.E.E. Fourth Edition, Re-written and Enlarged. London, New York, and Bombay: Longmans, Green, and Co. 1905.

The fourth edition of this work gives a complete account of the author's experience regarding the application of analytical processes to the elements and their compounds, their detection in minerals and ores, their extraction from various sources, and rapid methods of estimation suitable for use for commercial purposes, as well as more exact methods to be employed when extreme accuracy is a desideratum. The preparation and separation of the rare earths are included, together with an account of the most recent work that has been done on this subject. A chapter on Electrolytic Analysis and Gas Analysis describes the most accurate and convenient methods now in use, while another chapter is devoted to the consideration of miscel-

laneous processes, new methods and apparatus, and many special devices for economising time without sacrificing accuracy, as for example, in the shortening of filtering operations. The correct adjustment of weights, which is a subject often overlooked even when the highest degree of accuracy is desirable, as in the determination of atomic weights, is described fully, and tables are given for the mutual conversion of the decimal and English systems of weights and measures.

Researches on the Affinities of the Elements, and on the Causes of the Chemical Similarity or Dissimilarity of Elements and Compounds. By GEOFFREY MARTIN, B.Sc. (Lond.). London: J. and A. Churchill. 1905.

THIS work represents one of the first attempts to discover the relationships existing between chemical properties and atomic weight. For this purpose the author has investigated a great number of compounds, and has found that the affinities of the elements follow a definite "wave law," which he illustrates graphically by the construction of diagrams called affinity surfaces. These are made by plotting the positions of the elements according to the Periodic System on a plane surface, and erecting the perpendiculars through the point corresponding to each element, proportional to the attractive force which it exerts on the atoms of various other elements; the affinity surface is then the surface containing all the end points of these perpendiculars. Each element has a characteristic surface of its own, and allied elements have similar surfaces. One important conclusion among many others which the author draws from his work is that chemically similar elements attract the same radicles or atoms with proportional intensities of force. A vast amount of work must have been done in collecting the data for the book, and the author displays considerable originality of thought and ingenuity in arranging his facts, detecting relationships, and drawing conclusions, which make his book a valuable contribution to chemical literature. Some portions of it have already been published in a series of articles in the CHEMICAL NEWS, in which an abstract of the wave law and summaries of some of the important points in the argument were given.

A Three Years' Course of Practical Chemistry. By GEORGE H. MARTIN, M.A., F.C.S., and ELLIS JONES, M.A. First and Second Year. London: Rivingtons. 1905.

THESE two volumes provide a thoroughly satisfactory scheme for two years' work in elementary practical chemistry, and by the time the student has performed all the experiments and filled in the spaces in the book left for the description of processes and the drawing of conclusions, he will have prepared for himself a complete text-book of chemistry, containing his own experimental results. The preparation of the scheme has evidently been the work of teachers who are skilled in deciding exactly how best to draw out a boy's natural powers and to make his work interesting to him, and the students who use the book should become quite at home in all simple experimental manipulations, besides acquiring a very fair foundation for the knowledge of the principles of chemistry. While some parts of the authors' plan do not seem to be quite unexceptionable, the books will undoubtedly be found of real value, both by teachers and learners.

Die Elektrochemie der Organischen Verbindungen. ("The Electro-chemistry of the Organic Compounds"). By Dr. WALTHER LÖB. Third Edition. Halle-a-S.: Wilhelm Knapp. 1905.

THIS work is the third edition of the author's treatise on the electrolysis and the electro-synthesis of organic sub-

stances, which has been enlarged to such an extent as to necessitate a change of title. The subject matter has been re-written and re-arranged, so that the book now gives a complete survey of the application of electrolytic processes in the region of organic chemistry, and a discussion of methods and appliances used in electro-chemical research, while considerable space is allotted to the consideration of electro-thermic processes and of the silent electric discharge, the last subject being treated in a specially stimulating manner. The author considers his subject both from the practical and theoretical points of view, and describes fully the methods applied, the apparatus used, and the results obtained when electrical energy is employed used to bring about organic reactions.

Engineering Chemistry: a Manual of Quantitative Chemical Analysis. Third Edition. By THOMAS B. STILLMAN, M.Sc., Ph.D. Easton, Pa.: Chemical Publishing Co. 1905.

THE most important additions contained in the third edition of this work relate to the composition, commercial uses, and analysis of asphalt, the examination of lubricating oils and Portland cement, and the technology of the products of the blast-furnace. Besides the addition of this new matter, the whole of the text has been revised in accordance with our latest knowledge of the most rapid and accurate methods of quantitative technical analysis, and for use as a work of reference the book will be found to contain in a compressed form a large amount of information regarding general technical analysis.

CORRESPONDENCE

THE CHEMICAL CONDITIONS OF ELEMENTS.

To the Editor of the Chemical News.

SIR,—Just as in geometry there exists to every theorem concerning lines another theorem where the lines are replaced by points, so, also, in chemistry there exists to every theorem concerning the molecular state of matter another theorem concerning the sub-atomic state of matter. For example, there exist three states of matter of a molecular scale of magnitude—namely, the solid, liquid, and gaseous states; so, also, there exist three states of matter of a sub-atomic scale of magnitude—namely, the non-metallic, metallic, and radio-active states of matter.

In the non-metallic state the electrons oscillate about fixed centres in the body (compare the solid state, in which the molecules oscillate about fixed centres). In the metallic state the electrons are not confined to fixed centres in the body, but possess a freedom of movement within the limits of the body (compare the liquid state, in which the molecules move freely within the liquid, but do not travel outside its limits). In the radio-active state the electrons travel about in all directions, and are not confined to the limits of the body (compare the gaseous state, in which the molecules are not confined to the limits of the body, but travel about in all directions).

Just as any influence which steadily increases the motion of the molecules causes a body to steadily pass successively through the three molecular states—viz., the solid, liquid, and gaseous states—so, also, any influence which steadily increases the motion of the electrons within a body also probably causes it to pass from the non-metallic to the metallic, and finally into the radio-active condition.

So that the chemical state which a given element finds itself in at ordinary temperatures is probably only a phase or condition which other elements could also assume by suitably altering the external physical conditions under which they are viewed—a conclusion which I had pre-

viciously arrived at, but from other considerations (see the writer's work, "Researches on the Affinities of the Elements," pp. 207-240, Churchill, London, 1905; also CHEMICAL NEWS, lxxxiii., 130; lxxxv., 205, 310; lxxxvi., 295; lxxxvii., 74, 162).—I am, &c.,

GEOFFREY MARTIN.

University of Kiel, October 15, 1905.

MISCELLANEOUS.

British Science Guild.—The Inaugural Meeting of this Guild, held at the Mansion House, has had the effect of largely increasing the list of applications for membership. Sir Norman Lockyer desires it to be known that would-be members should apply for particulars to the Honorary Secretary, 16, Pen-y-Wern Road, S.W.

Royal Institution.—A General Monthly Meeting of the members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President in the Chair. Lady Alford, Mr. W. Friedlander, Dr. A. Muirhead, and Mr. D. A. Thomson were elected Members. The Special Thanks of the Members were returned to Mr. Robert Hannah for his gift of the picture, painted by him, of "Master Isaac Newton in his Garden at Woolsthorpe, in the Autumn of 1665."

Appointments.—Dr. Alexander McKenzie, M.A., D.Sc. (St. Andrews), Ph.D. (Berlin), Lecturer and Senior Demonstrator in the University of Birmingham, has been appointed Head of the Chemical Department at the Birkbeck College in succession to Dr. John E. Mackenzie, D.Sc. (Edinburgh), Ph.D. (Strasbourg), who has accepted the appointment of Principal of the Technical Institute, Bombay.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Saccharin.—I am desirous of ascertaining particulars of the manufacture of saccharine (süsstoffe), and whether that chemical is being manufactured in England in a liquid form.—M. C.

MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Microscopical, 8. Exhibition of Microscope Slides of Tsetse Fly Dissections, Trypanosomes, &c.

Society of Arts, 8. Inaugural Address of the 152nd Session, by Sir Owen Roberts, M.A.

THURSDAY, 16th.—Chemical, 8.30. "Silicon Researches—Part IX, Bromination of Silico-phenyl Imide and Amide, and formation of a Compound including (SiN)—" by J. E. Reynolds. "Condensation of Ketones with Mercury Cyanide," by J. E. Marsh and R. de J. F. Strubbers. "Application of the Microscopic Method of Molecular Weight Determination to High-boiling Solvents," by G. Barger and A. J. Ewins. "Green Compounds of Cobalt produced by Oxidizing Agents," by R. G. Derrant. "Synthesis of Tertiary Menthol and of Inactive Menthone," by W. H. Perkin, jun. "Optically Active Reduced Naphthoic Acid—Part I, Dextro- Δ^2 or 3-dihydro-1-naphthoic Acid," by R. H. Pickard and A. Neville.

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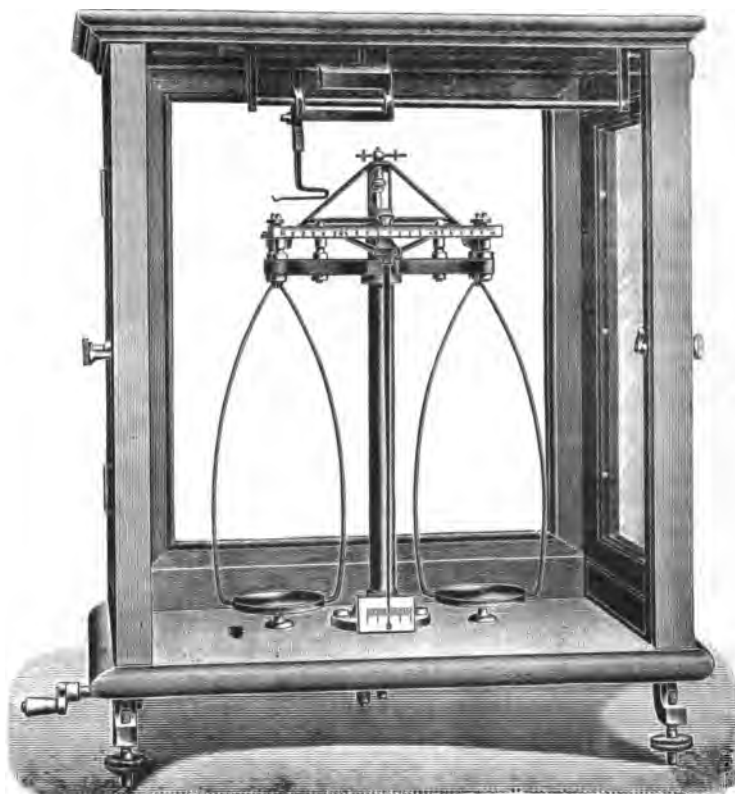
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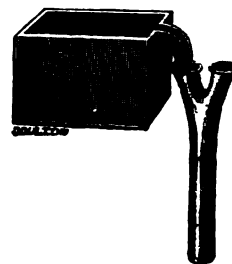
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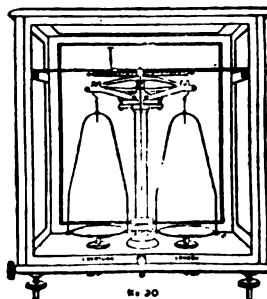
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THE

THEORY OF PHOTOGRAPHIC PROCESSES.*

PART II.—ON THE CHEMICAL DYNAMICS OF DEVELOPMENT, INCLUDING THE MICROSCOPY OF THE IMAGE.

By S. E. SHEPPARD, B.Sc., and C. E. K. MEES, B.Sc.

THE investigation of development described in a previous communication was extended by the application of microscopic methods (*Proc. Roy. Soc.*, lxxiv., pp. 447 to 473). The fact that both the silver haloid and the resulting silver are distributed through the film in the form of particles of minute but measurable size, allows us in this way to detect finer qualitative differences in, and to draw independent deductions on, the processes of exposure and development. The size of the grain is important, both from the practical point of view and from the theoretical, in the one case as bearing on spectroscopical and astronomical photography, in the other on account of the great importance of the degree of surface-extension for heterogeneous systems (Ostwald, "Lehrbuch," vol. iii., "Chem. Kinetik."; Bredig, *Arch. f. Wiss. Phot.*, 1900; "Eder's Jahrbuch," 1899, p. 357).

The method has been used previously by Abney, Abegg, Kaiserling, Ebert, and others (H. Ebert, "Eder's Jahrbuch," 1894, p. 14; Kaiserling, "Phot. Mit.," 1898, i. and ii.; Abney, *Phot. Journ.*, 1898; R. Abegg, *Arch. f. Wiss. Phot.*, 1899, vol. i., p. 109), but by far the most systematic and important inquiry is that of K. Schaum and V. Bellach (*Phys. Zeit.*, 1901-02; and especially "Die Struktur der Phot. Negative," by V. Bellach—W. Knapp, Halle, 1903; this admirable monograph contains a very complete bibliography on all points).

The work subsequently described had been carried out in part before Bellach's monograph came to our notice. The investigation was then extended beyond the limits of exposure and development given by Bellach (except in region of solarisation), and arranged to compare both with his results and those of our former paper. As much of the detail is of chiefly photo-technical interest, only the chief results are given here; a fuller account will be published in the *Photographic Journal*.

Experimental.

Beck objective $\frac{1}{4}$ -inch and Reichart No. 8 $\frac{1}{8}$ -inch, both dry systems, and for some work Zeiss $\frac{1}{8}$ -inch cedar-oil immersion, kindly lent by Professor A. W. Porter, B.Sc. The micrometers were a stage-micrometer in $\frac{1}{10}$ m.m., an ocular calibrated on this, and an ocular in squares similarly calibrated.

Emulsion Tests.—As the study of ripening was deferred for further work, only the points bearing on the theory of development were considered. Preparations were made by dissolving a small piece of film in warm water and flattening under a cover-glass, then sealing with Canada balsam. The grains of a very thin layer thus obtained could be examined separately. Long exposure had no apparent effect.

The grain in fast plates varied somewhat in size, there being, e.g., in an Imperial Special Rapid, two species—(a) 0.0011 m.m. and (b) 0.0034 m.m. The latter were flattened polyhedra, of triangular section; in the slow plates the emulsion was practically homogeneous, the size of grain in Wratten ordinary being in mean 0.0017 m.m. It could not be ascertained with certainty whether the grain was crystalline or amorphous.

The Physical Nature of Silver Haloid Emulsions.—Bellach (*loc. cit.*, p. 34) found that in many cases the mean size of the grain diminished with careful drying. Thus, after several days' desiccation, a contraction from 0.67×10^{-5} m.m. to 0.57×10^{-5} m.m. was noticed in an Eder emulsion. This points to the grain itself possessing structure, and agrees with Quincke's views as to the nature of silver haloid emulsions (*Ann. d. Phys.*, [4], ii., 1000 *et seq.*). He considers that the AgBr "grains" are not pure AgBr, but contain gelatin. An emulsion in which the colloidal particles have flocked together forms a "spume." Liquid or jellified colloids consist of "spume" masses with liquid or solid spume-walls, enclosing very minute or invisible chambers. In haloid emulsions there is a stiff jelly containing a totally or partially solidified solution of AgBr in gelatin, in which a phase rich in AgBr has separated from a second phase poorer in AgBr, but richer in gelatin (Hardy, *Zeit. Phys. Chem.*, vol. xxx.). In the spume-walls and cells, spheres and crystals of haloid, much smaller than the measured grain, have separated.

The "adsorption" of gelatin to the AgBr agrees with Eder's researches on the separation of pure AgBr from emulsions by centrifugalising (Eder and Valenta, *Beitrag zur Photochemie*, &c., Sec. 3, p. 19).

Structure of Developed Negative.

By focussing on the top layer of particles, then down on to the lowest observable particles, the thickness of the reduced silver layer can be measured. This apparent thickness, recorded by the micrometer head of the fine adjustment, and multiplied by n_1/n_2 , these being respectively the refractive indices of the gelatin and objective systems, gives the real thickness (Bellach, *loc. cit.*, p. 56).

With Wratten ordinary emulsion, exposed and developed as described, the negative layer was somewhat as described by Bellach:—

- Surface-area, particles not very numerous.
- Mean-layer, with characteristic forms.
- Lower zone of smaller particles, diminishing the lower they lie. This Bellach attributes to the penetration of developer, but we shall show later that a more potent factor is that the most exposed grains start development first. On ultimate development these grains reach the same size as the others.

For the thickness, the following facts were ascertained:—

- With constant development for a short time the depth of the image is independent of the exposure.
- With increased time of development the depth increases rapidly to a maximum for each exposure, after which it is constant.
- With long development the depth increases somewhat with the exposure, a limit naturally being fixed by the thickness of the film.

TABLE I.—N/10 Ferrous Oxalate.

Two minutes at 20° C.			Ten minutes at 20° C.		
No.	Exposure. C.M.S.	Thickness. M.m.	No.	Exposure. C.M.S.	Thickness. M.m.
2.	2.04	0.0226	1.	0.101	0.0115
3.	4.66	0.0223	2.	0.204	0.0116
4.	7.75	0.0221	3.	0.466	0.0118
5.	12.9	0.0223	4.	0.775	0.0139
6.	27.9	0.0230	5.	1.290	0.0195
7.	54.5	0.0255	6.	2.790	0.0232
8.	113.0	0.0241			

TABLE II.—N/10 Ferrous Oxalate. Time of Development and Thickness. Exposure = 1.38 C.M.S.

Time. Minutes.	Density, D.	Thickness. M.m.
2.0	0.130	0.0200
6.0	0.280	0.0207
8.0	0.349	0.0206
10.0	0.542	0.0203
∞	0.586	0.0203

* A Paper read before the Royal Society, March 30, 1905.

Every measurement is the mean of ten, each focussing being repeated, and for various portions of the film.

On the Size of the Grain.

Many discordant observations as to the influence of exposure and development on the size of the grain have been published (Bellach, *loc. cit.*, p. 72). Our observations agree with Schaum and Bellach's for the early stages of development, but on prolonging the development the conclusions are modified. They may be expressed as follows:—

When γ , the degree of development, is low, the size of grain increases with the exposure.

As the time of development increases, the size of the grain does also, until at γ_{∞} it is independent of the exposure.

In addition to micrometric measurement of the diameter, the mean size was obtained by drawing the outline of the grains on squared paper by means of a reflecting system (*Ibid.*, p. 76), and then measuring the surface-extension. This method could not be applied to the smallest grains, for which the micrometric measurements are only approximate. The mean diameter of the "area" method is the mean between greatest and least, and is given to compare with the micrometric diameter. The results are the means of twenty observations and of ten for the area method.

Influence of Exposure.

TABLE III.—Developed Two Minutes in N/10 Ferrous Oxalate at 20° C.

No.	Exposure. C.M.S.	Micrometric diameter. M.m.	Area. M.m. ² .	Mean diameter. M.m.
		M.m.	M.m. ² .	M.m.
1.	1'03	0'00114	1'23 × 10 ⁻⁶	0'00101
2.	1'87	0'00112	1'45	0'00121
3.	3'10	0'00124	1'35	0'00123
4.	5'17	0'00135	1'82	0'00130
5.	11'8	0'00140	1'90	0'00152
6.	22'0	0'00162	2'10	0'00182

Mg = C. 920.

Mg = C. 1360.

For the exposure an intensity scale was used with constant time. Similar results were obtained by varying the time with intensity constant.

Influence of Development.

TABLE IV.—Exposure 1'38 C.M.S. Developed in N/10 Ferrous Oxalate at 20° C.

Time. Minutes.	Density.	Micro diameter (a).		Diameter (b).	
		M.m.	M.m. ² .	M.m.	M.m. ² .
2'0	0'150	0'00103	0'0008	0'0010	0'0010
6'0	0'280	0'00124	0'0010	0'0014	0'0016
8'0	0'349	0'00157	0'0016	0'0017	0'0017
16'0	0'542	0'00160	0'0016	0'0017	0'0017
∞	0'586	0'00167	0'0017	0'0017	0'0017

(a) For mean layer.

(b) For lower zone.

Size of Grain on Infinite Development.

For moderately high exposures and prolonged development measurements could not be made on the plate direct, so preparations were made and the grain measured and photographed.

TABLE V.—Developed to γ_{∞} in N/12'5 Ferrous Oxalate.

Exposure. C.M.S.	Density.	Micro-diameter.		Diameter.	
		M.m.	M.m. ² .	M.m.	M.m. ² .
2'04	0'277	0'00145	1'94 × 10 ⁻⁶	0'00135	0'00165
4'66	0'966	0'00150	2'17	0'00152	0'00171
7'75	1'496	0'00137	1'90	0'00159	0'00165
12'90	2'400	0'00156	2'14	0'00156	0'00140
27'90	3'400	0'00149	1'90	2'18	2'03
54'30	4'39	0'00151	2'18	0'00156	0'00156
209'0	—	0'00140	2'03	0'00156	0'00156

Hence, generally, $G = \phi(\gamma, E)$, but at γ_{∞} G is independent of E , the exposure.

Effect of Bromide.

TABLE VI.

No.	Exposure. C.M.S.	Diameter A. M.m.	Diameter B. M.m.
		M.m.	M.m.
1.	1'01	0'0009	Absent
2.	2'04	0'00094	Points
3.	4'66	0'00105	Points
4.	7'75	0'00114	0'0008
5.	12'90	—	0'00085
6.	27'9	0'0143 (a)	0'00103
7.	54'5	—	0'00123
8.	113'0	0'0165 (a)	0'00145

(a) From preparations.

These were developed 1'0 minutes in N/10 ferrous oxalate. A, no bromide; B, N/200 KBr.

This confirms Bellach's statement that bromide lowers the size of the grain. In addition, it should be noticed that the effect is greater the less the exposure. Also, it was found that the size of the grain diminished as the concentration of the bromide increased.

Bromide at Infinite Development.

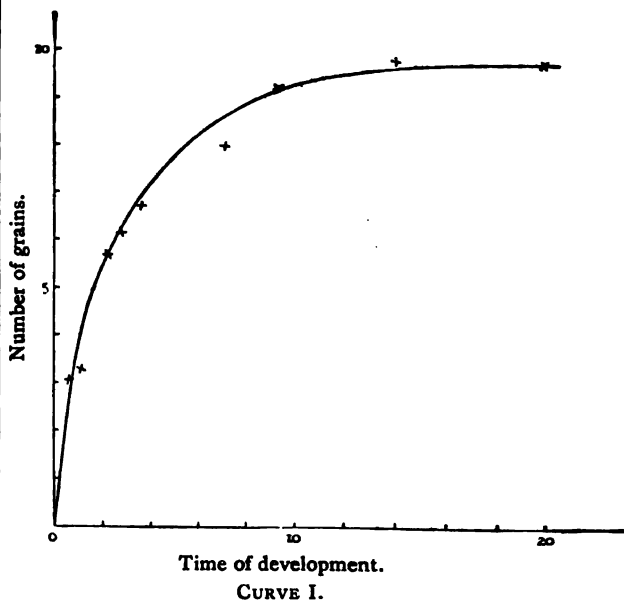
TABLE VII.—Developed to γ_{∞} in N/10 Ferrous Oxalate, N/200 KBr.

No.	Exposure. C.M.S.	Micro-diameter.		Mean diameter.	
		M.m.	M.m. ² .	M.m.	M.m. ² .
1.	2'04	0'00142	1'7 × 10 ⁻⁶	0'00135	0'00142
5.	27'9	0'00137	1'9	0'00142	0'00139
8.	209'0	0'00172	2'0	0'00139	0'00139

Mg = 920.

Mg = 1300.

On comparing this table with Table V., it will be seen that, on infinite development, the grain attains the same size in a bromided as in a non-bromided developer.



On the Number of Grains and Exposure.

In the Surface Area.—For this, photo-micrographs were taken at 500 diameters, and the grains counted in a given area on the negative. The values are the mean of twenty observations.

TABLE VIII.—Developed Ten Minutes in N/10 Ferrous Oxalate.

No.	Exposure, C.M.S.	No. per visual area.	No. per 1 m.m. ² film.
2.	0.187	17.1	192 × 10 ²
3.	0.310	16.2	181
4.	0.517	18.8	211
5.	1.18	17.8	199

Hence for moderately long development, the number of grains on the surface is constant.

In the Thickness.—These were counted directly under the microscope, with a micrometer in squares. The values are for 25 to 30 squares, readings being taken in different portions of the film. The unit volume is a prism of area 1 m.m.² and height equal to thickness of film. It was found that the number of grains increased with the exposure and for moderately long development was nearly proportional to the density. As this is contrary to Bellach's results, several sets of experiments were made, with as wide a range as practicable of exposure and development, which fully bore this out. The conclusion was further tested by making sections through the film. The best results were obtained by removing the developed film from the plate and rolling it up in gum mucilage. A small portion was then frozen on an ether spray microtome and sections cut. These gave a spiral embracing several tones, and it was easily seen that the number of grains increased with the exposure, the depth of the image but slightly. The appearance agreed with Abney's description (*Phot. Journal*, 1898):—"With small exposure the grains are congregated chiefly near the surface. As the exposure increases, the film behind fills up with particles and they crowd together."

TABLE X.—Developed Six Minutes in N/10 Ferrous Oxalate.

No.	Exposure, C.M.S.	No. per 100 m.m. ² visual.	Per unit vol.
1.	0.04	2.90	27.3 × 10 ³
2.	0.081	2.46	23.4
3.	0.184	3.21	30.2
4.	0.312	6.10	57.5
5.	0.52	7.58	71.0
6.	1.12	8.34	78.5

Mg = C. 1000.

1 and 2 were below the "Schwellenwerth." Obviously the number increases with the exposure. This was confirmed for other experiments, as far as the density permitted. Above 0.3 to 0.4 measurements could not be made; but it can be seen that on extreme development (Table V.) the size of the grain is constant. Yet the density has increased from 0.277 to 4.39, or about sixteen times. Since no commensurate increase in the size of the grain has occurred, the number must have increased.

Influence of Development.

TABLE X.—Wratten Ordinary Plate Exposed for 0.25 C.M.S. Developed in N/10 Ferrous Oxalate at 20° C.

No.	Time, minutes.	No. of grains per 100 m.m. ² visual.	Per unit vol.
1.	0.5	3.35	31.5 × 10 ³
2.	1.0	3.54	33.3
3.	2.0	6.10	57.5
4.	2.5	6.45	62.5
5.	3.5	7.20	67.8
6.	7.0	8.58	80.8
7.	9.0	10.03	94.5
8.	14.0	10.50	99.0
9.	20.0	10.40	98.9

See Curve I.

The number of grains increases rapidly at first, then more gradually until a maximum is attained. This agrees with Bellach's results.

(To be continued).

THE SOLUTION STATE.

By W. P. DREAPER, F.I.C.

OBJECTIONS have been raised to the dissociation theory originally put forward by Arrhenius on the grounds that the conditions suggested by the same are of an arbitrary nature.

It is assumed that without any counteracting force coming into play, the molecules of the solute dissociate into inter-groups or ions, positively and negatively charged, which migrate freely in an inert medium.

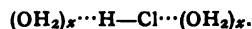
On somewhat similar lines it is perhaps possible to take exception to the modified hydrate theory recently advanced by Dr. Lowry (*Proc. Faraday Soc.*, 1905, p. 1), on the grounds that it also does not allow the possibility of any continuing action of a primary nature in this solution state.

Prof. Armstrong's suggestion that the association of the solvent molecules takes place between the solvent molecules and the negative radicals of the solute does not seem to fall in with Faraday's original proposition, when he assumed some attractive force between the opposite radicals in any two compounds.

Prof. Armstrong further suggested that the process of ionisation, as represented by this action of association, does not involve the splitting up of the molecule into separate ions.

In considering the general action of dyeing, the writer suggested a theory of solution as an alternative one, and which does not seem to entail the isolation of the hydrated ions as suggested in Dr. Lowry's later theory. It may be extended also to cover the pseudo-solution state when the modified actions are of special interest. It differs from either of the above theories or that of Brühl in assuming a constant state of equilibrium between the attractive force of the atoms in the molecule, on the one hand, and those in their total or individual effect, and the molecules of the solute on the other, or the intra-groups of the same as the case may be.

In proposing a theory to explain the general action of dyeing (*Journ. Soc. Chem. Inst.*, 1905, p. 223; and *Journ. Soc. Dyers and Colourists*, 1905, p. 136), the following example was given to illustrate the supposed action, viz.:



The association of 2x molecules of water with one molecule of hydrochloric acid is assumed to correspondingly weaken or reduce the primary bond between the H and Cl atoms, each atomic unit being under the direct influence of the solvent molecules and not the negative one only as suggested by Dr. Armstrong.

This seems to be the necessary adjunct to Faraday's law that the opposite ions will attract one another, if we assume, as I did, that the primary and secondary attractions are of the same order and interchangeable.

This action is of a different order to the one more recently suggested by Dr. Lowry (*Ibid.*), viz.,—



which assumes the hypothetical formation of ionic hydrates on lines similar to the biological process of Karyokinesis. Here we have no evidence that the primary bond is still in existence. The system is an isolated one. The two atomic units, K and Cl, are independent; the primary attraction between them is entirely replaced by that of the $-(\text{OH}_2)_x$ groups as represented by their respective atomic units.

In order to explain this action, I assumed that under certain conditions the total attractive force exerted by the atomic unit A is constant, and that in the presence of the solvent molecules and by reason of their secondary or molecular attraction, the primary bond is correspondingly reduced in intensity.

This may be roughly indicated in the following way:—

If x = primary attraction and y = the secondary attraction, then—

$$A - x - A'$$

will become—

$$S_y \cdots A - (x - y) - A' \cdots S_y$$

in the presence of the solvents' molecules, S_{2y} . As y increases in intensity and the ratio of S molecule to $(A - A')$ increases, so the primary bond x will decrease in value.

In a corresponding way, and as x decreases in value, so may the chemical activity of A and A' increase. Thus solutions of mineral acids may react where the pure acid is inactive.

This solution state of the solute molecules would, from this point of view, be equivalent to a certain percentage of the units A and A' being in a free state, but actual disintegration of the molecule $(A - A')$, as assumed by Arrhenius, on the one hand or by Dr. Lowry on the other, may not be a necessary consequence of this solution state.

Under this reduced condition of primary attraction it is also assumed that atomic migration may correspondingly increase, and this would probably tend to increase the activity of the units.

From this point of view, therefore, the activity of the solute molecules will be due to the state of strain set up when x becomes $x - y$, and to the increased rate of atomic migration.

A balance between the primary and secondary attraction is set up, but y is never so great that $x - y$ becomes a negative value or is even reduced to zero; the units A and A' will always remain within the range of their respective attraction.

This action also would, except under the influence of external surface attraction, set up or tend to set up a condition of equal strain over the entire system whether the solute be in a state of solution or pseudo-solution, and not an unequal one under which the separation of some of the solute molecules into atomic groups or ions, hydrated or otherwise, is indicated.

I also assumed that the primary and secondary attraction of A are of the same order, and that the secondary attraction may be identical with molecular attraction, which at close quarters is known to be very great, and that if the molecular system is broken down it must be by some force equivalent to, or greater than, the primary bond. That such a condition of strain may explain how a "dissociation effect" may be observed in dilute solutions and an "association effect" in more concentrated ones without assuming the total suppression of the primary bond, which would render the perfectly reversible nature of solution more difficult to understand.

Also that, if this is so, the forces which we recognise as atomic and molecular are unified and brought within the range of the phenomena which we associate with gravity, it being always remembered that an intensification of Newton's law is necessary to explain the molecular effect at close quarters.

This unexplained intensity may possibly be due to the transfer of primary into secondary attraction, and may be an indication of the possible range within which this action may take place.

As suggested further on, definite sub-systems may form in the solution system, which may lead to the formation of hydrates or definite but complex aggregates. In such a case this system should be regarded as a two-phase one in the same sense that a hydrogel is considered to be one.

This hypothesis agrees with the assumed conditions of the state of pseudo-solutions put forward to explain the facts recorded in the original paper.

If we allow that (1) within certain limits of concentration, and when once an equilibrium is established, and where the action is a reversible one, the aggregates in any solution are of equal size, and (2) the aggregates in a stronger pseudo-solution are larger in direct relation to the number of molecules (of the solute) present, and when

once a certain point is reached they increase in size rather than number; and that this solution state is assumed to be the result of the equilibrium between these respective attractive forces.

Then the conditions which exist and cause the alterations in the freezing- and boiling-points of the solvent on addition of the solute may possibly be explained in this way from one end of the solution scale to the other.

If we assume that the ionic effect is produced by the partial separation of the solvent molecules as indicated by the ionic hydrate theory, we have no explanation why the remaining solution molecules do not behave in a normal way.

The reversal of the action, too, in strong solutions will be due to the more definite grouping due to molecular hydration, in the same way that pseudo-solutions form hydrogels. It seems natural that in stronger solutions, where the solute molecules are in closer contact, that their mutual attraction will correspondingly increase, especially as at the same time the ratio of the molecules of the solution to solute decreases. This will bring about an increasing tendency for what may be called "grouping," in which the proportion of solute molecules in the complex will naturally increase.

Conductivity of Solutions.—It is generally assumed that the passage of a current is due to the presence of free ions. The passage of surcharged ions carrying with them innumerable associated molecules of water is a difficult one to conceive.

It may be mentioned here also that certain colour changes which have been attributed to the presence of free ions will take place where dissociation is said to be absent (Kahlenberg, *Trans. Faraday Soc.*, 1905). Is it not as reasonable to assume that association effects of a certain kind may afford free paths for the electrical distribution of energy through space?

If we consider a hypothetical system of linking as indicated—

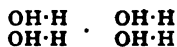


we arrive at a possible free path for energy and even possible lines of atomic migration of an abnormal character in the presence of an independent flow of electrical energy.

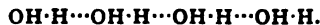
As x decreases in value the rate of flow would be facilitated by the formation of a number of extra free paths.

The colour effects produced may be due to the condition of strain $A - A'$ rather than to the ionic effect.

Dr. Lowry says "the affinity of water molecules for H and OH must be relatively slight, since otherwise liquid water would be a good conductor." Yet water is generally regarded as an associated liquid. It may be that the aggregates are grouped rather than linked up in this case.



may represent the condition rather than—



It is necessary to point out that this chain hypothesis is different to the Grothaus one. In the latter case it was assumed that the breaking down of the chain was necessary before electrolysis could take place, and that a certain electromotive force was necessary to accomplish this. Further work has shown that this is not so when the poles are of the same metal as that of the salt in solution.

The "chaining up" of the associated molecules is suggested as the cause of the conducting power of the so-called electrolytes.

When this is absent the solution is a non-conductor. Association in this case means grouping such as we presumably get in pseudo-solutions.

The superior conducting power of solutions at higher temperatures may be due to some such change in the solution state.

It has been pointed out (*Elect. Review*, 1905) that it is an essential postulate of the "hydrate" theory of Dr. Lowry

that the ions have a greater affinity for the solvent molecules than for their companion ions.

I pointed out (*Ibid.*) that, owing to the very close quarters at which the molecular attraction increases abnormally, it is not likely that the combined pull of the solvent molecules would ever altogether displace the primary bond by direct substitution. At the same time we have no direct means of measuring the relative values of S_y and x .

It has also been pointed out that Dr. Lowry's theory does not explain the motive or reason why the solvent has this greater affinity for ions than molecules.

The term electrolyte is also of an indefinite nature. In a mixture of acetic acid and water which is the electrolyte? Neither of these solutions will conduct in the pure state. The inference is that free ions are only present in mixtures. The conditions of atomic migration would seem to apply to pure solutions. This would not conform with any theory of atomic isolation as the cause of these phenomena in solutions.

Dr. Lowry is of opinion that at low concentrations the greater part of the salt must be in an "ionised" condition, and the experimental data are fully in accord with the view that combination with the solvent is characteristic of the ion even more than the molecule.

From the point of view that the action may always be referred to the atomic units themselves this would agree with the above views. However, granted that the primary and secondary attractions are identical so far as their origin is concerned, it would seem natural to assume that the primary bond will always be the stronger, and that this would prevent ionisation.

If we assume that the partial or selective action takes place, leading to the isolation of ions or molecules of the solute and their removal from the active sphere of the solution, it must be remembered that in similar conditions in pseudo-solutions, where some such grouping undoubtedly takes place, the influence of the salt on the solution and its physical constants is reduced.

Why, if 1 molecule of any substance be dissolved in 100 molecules of a liquid of a different nature the lowering of the freezing-point is nearly constant, and that if an ion corresponds with a molecule in its influence that a value of double the original factor (0.63°) will indicate dissociation into two ionic groups, or three as the case may be, and that these higher figures have been recorded in some cases, is held to indicate dissociation.

Why should not these abnormal figures equally well indicate association (in weaker solutions) to a correspondingly increased extent? In this case it would be assumed that double the number of solvent molecules would be held in association, and that in stronger solutions, where the ratio of solute to solution would be in favour of the former, this phenomenon would give place to a more simple association effect for want of sufficient molecules of the solution to go round.

The explanation offered by Jones and Chambers (*Am. Chem. Journ.*, xxiii., 103), that in the case of abnormal cases in freezing-point experiments with substances which are hygroscopic, the solute combines with large numbers of solvent molecules and removes them from the sphere of action, hardly explains why the other and remaining solvent molecules which are still in the sphere of action, do not act in the normal way. If, however, we assume in this case that the action is a general but abnormal one of attraction between the solvent and solute molecules, it is held that it is easier to assume that association is the cause of this abnormal action in so-called hygroscopic bodies than that it is due to ionic splitting, when it is remembered that in the hygroscopic action of the salts themselves on exposure to air (moist) the attacked solution will be in a very concentrated form and not in a favourable condition for ionisation, it being remembered that it is the same hygroscopic substances which give abnormal results in more dilute solutions as noticed above.

Saturation-point.—A solution will become saturated

when an equilibrium is established between unit mass of the solution and a further mass of the solute. The attraction of the solution for the solute will fall to zero at this point. In the case of pseudo-solutions when the action is complicated by the production of aggregates of the solute, either alone or in conjunction with solvent molecules, the presence of a more soluble salt will displace the solute. This is seen in the "salting out" of colloids.

Again, as Kahlenberg has pointed out, the ionic theory in its application to the precipitation of colloids breaks down. The attempts to ascribe the precipitation to the presence of free ions which the precipitating electrolyte is supposed to supply, are discounted by the fact that the power of coagulating colloids is not confined to electrolytes.

In conclusion, therefore, it is suggested that the balance between the two forces which we call molecular and atomic respectively may explain the phenomena met with in solutions of crystalloids or colloids in a more satisfactory way than assuming the formation of "hydrated ions" on the one hand, or the isolation of ions in a negative medium on the other. It is necessary, however, to assume that these two forces are really one and the same, the difference being one of degree; that the intensification of Newton's law at close quarters is due to the weakening of the primary bond and consequent increase in the effective and rapidly increasing attraction between molecule and molecule at close quarters, due to the transfer of primary into secondary attraction.

The presence of hydrates or definite solution solute aggregates is a secondary matter. The conductivity of a solution depends on the "linking up" of solution and solute molecules. The increased "activity" of the solute in solution is due to this weakening of the primary bond and possibly the consequent increase in atomic migration.

In solutions which do not conduct the "linking up" is replaced by "grouping" of a similar nature to that seen in pseudo-solutions. This is caused by the attraction of the solute molecules for one another being relatively greater than that of the solution molecules for the solute.

The presence of a larger series of hydrates is also of a more complicated nature than that of general association, which at certain points may lead to such marked grouping effects that they persist into the solid state.

Roscoe's experiments on the indifferent points in solutions confirming the idea that definite hydrates were not formed, shows that the relation between solvent and solute is a more closely balanced and reversible action than that indicated by the term hydration. Variations of such outside influences as reduction in atmospheric pressure had a marked effect on the experimental results obtained. Such a delicately adjusted equilibrium between the solvent and solute as that indicated, and which is subject to slight variations in the vapour pressure of the latter, hardly indicates the formation of definite compounds.

The production of eutectic mixtures also indicates a very loose attraction between the solvent and solute. But in both cases and under standard conditions this balance is so set up that in the one case the solute and solvent will distil together in constant ratio, and in the other they will be thrown out of the system in the solid state in a definite but independent ratio.

In conclusion, therefore, it is suggested that in the present incomplete state of our knowledge there is as much evidence in favour of the above modified association theory as there is in favour of the one which assumes the presence of "hydrated" ions.

Also that if we assume these conditions we may possibly find in them some explanation of the different phenomena exhibited in the three states of matter. In the liquid form the molecules have so far approached each other that the transfer of the primary attraction into secondary attraction is coming into play, but is not yet sufficient to prevent molecular migration.

In the solid state the transfer is more complete, and an actual linking may take place, and an internal condition of

strain set up which may account for the different conditions set up in solids as shown by our physical measurements.

Also molecular migration is slowed down or even entirely prevented, as is seen in the well known experiments on this subject.

This transfer similarly explains the abnormal attraction at short distances as exhibited in nature which is said to be greatly in excess of that required by Newton's law.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

(Continued from p. 222).

ONE hundred grms. of the residues obtained by the evaporation of mother-liquors (see p. 221) to dryness were dissolved in water and fractionally crystallised. After having removed as much of the tantalum as possible by introducing dilute potassium hydroxide into the boiling solution until a rather considerable and permanent precipitate was obtained, the solution was boiled for some time. The first fraction of crystals (2) and the third fraction of crystals (3) were removed, after which hydrofluoric acid was added to the mother-liquor, from which there separated a crop of needles, which we shall designate Crystals 4. These last were re-crystallised from hydrofluoric acid. They probably contained silicon and tantalum. The acid mother-liquors from these different crops of crystals were treated as described by Hermann (*Journ. Prakt. Chem.*, 1877, [2], xv., 105); that is, they were treated with 20 parts or 2 litres of water and 150 grms. of sodium hydroxide. A clear solution resulted, from which a fine crystalline precipitate separated. The filtrate from this precipitate gave no reduction test when treated with acid and zinc, nor was anything obtained from it after having added dilute sulphuric acid and a slight excess of ammonium hydroxide. It was free from earthy bases and metallic acids.

The crystals of the sodium salt (2.5 grms.), obtained as outlined in the last paragraph, dissolved almost completely in 20 parts of boiling water, and separated in well-defined forms from the cold solution. A portion of this salt heated in a salt of phosphorus bead imparted a blue colour to the latter in the reducing flame.

The next step was to decompose the solution of this crystalline sodium salt with dilute sulphuric acid. The solution was hot. The precipitate which separated was thrown upon a filter and washed, after which it was dissolved in hydrofluoric acid and an equivalent amount of potassium carbonate added in order to form potassium-columbium oxyfluoride. The solution was evaporated to dryness upon a water-bath, the residue repeatedly moistened, and evaporation to dryness repeated until the odour of hydrofluoric acid could not be detected by the smell; then the salt was baked, taken up in water, and the solution boiled for some time. A trace of tantalum oxyfluoride separated. It was filtered out. On evaporation to crystallisation the leafy characteristic crystals of potassium-columbium oxyfluoride appeared. They were dried between bibulous paper and then analysed.

Analysis.

0.5502 grm. of salt gave 0.2452 grm. of oxide and 0.3224 grm. of potassium sulphate.

0.2452 : 0.3224 :: $x/2$: 174 $x = 264.6$.

	Calculated, $K_2C_2O_5H_2O$.	Found.
Oxide	44.52	44.56
K_2SO_4	57.81	58.60

A portion of crystals No. 4 was re-crystallised and analysed.

Analysis of Re-crystallised portion of Crystals 4.

0.5588 grm. of sample gave 0.2407 grm. of oxide and 0.3232 grm. of potassium sulphate.

0.2407 : 0.3232 :: $x/2$: 174 $x = 259.2$.

	Calculated, $K_2C_2O_5$.	Found.
Oxide	43.93	43.08
K_2SO_4	57.05	57.84

The results of analysis as well as the behaviour points to the fact that the oxide contained in these residues is mainly columbium oxide, Cb_2O_5 , with a small portion of another oxide causing the equivalent weights obtained to be too low. These results may in part be due to the presence of some potassium silicofluoride, but more likely to potassium-titanium fluoride. Yet these last fractions of double fluoride in which the titanium should be concentrated show only very small amounts. Starting with so much material the last fractions should show more titanium if it is present in the mineral in appreciable amounts.

The only test for small amounts of titanium which we have are the hydrogen peroxide test of Schönm (*Jahresberichte*, 1893, 901) and the chromotropic acid test used by Geisow ("Dissertation," 1902). Of these the former is the only one relied on, and it offers the only direct evidence which we have for the presence of titanium in the potassium-columbium oxyfluoride obtained from columbite.

The methods applicable in the preparation of columbium oxide relatively free from titanium are as follows:—

1. Crystallisation of potassium-columbium fluoride, $K_2C_2O_5$, which is not isomorphous with potassium titanium fluoride. The difficulty in this case is that the hydrofluoric acid increases the solubility of the columbium body and decreases that of the titanium double fluoride, so that the titanium would have less tendency to concentrate in the mother-liquors.

2. Fractional precipitation with dilute ammonium hydroxide. The columbium hydrate is precipitated first and the titanium concentrated in the last fractions. No fraction consists entirely of titanium hydrate; even the last fraction is largely columbium hydrate.

3. The formation of the chloride or oxychloride of columbium and the chloride of titanium and separating these by distillation.

4. Treatment of the hydrates with cold, fairly concentrated sulphuric acid, in which the titanium hydrate should dissolve and leave the columbium.

All of these methods were tried in the endeavour to obtain sufficient titanium from the columbium to identify it and prepare some of its derivatives, e.g., the potassium double fluoride. In order to try our Method 1 the remainder of the residues—2 to 3 kilos.—was crystallised twice from hydrofluoric acid, thus getting potassium columbium fluoride, $K_2C_2O_5$. The mother-liquors were united. They equalled 600 c.c. They were neutralised with dilute ammonium hydroxide; the precipitated hydrate filtered out and the filtrate made alkaline with a large excess of ammonium hydroxide, which gave a further precipitate. This last hydrate was filtered out and dissolved in hydrofluoric acid. Potassium carbonate was added and the solution evaporated to dryness on a water-bath, the residue taken up in water and crystallised. The crystals obtained were short stubby needles. They were evidently not potassium-columbium oxyfluoride, $K_2C_2O_5$. Their quantity was too small to re-crystallise, but they were analysed:—

0.4672 grm. of sample gave 0.1740 grm. of oxide = 37.6 per cent.

0.4672 grm. of sample gave 0.3050 grm. of K_2SO_4 = 65.3 per cent.

The specific gravity of the oxide was found to be 5.2, although too little of it was at hand for accurate work. The determination of the titanium in the oxide colorimetrically gave 0.0106 grm. of TiO_2 = 6.1 per cent.

* *Proceedings of the American Philosophical Society*, 1905, xlv., p. 177.

The salt originally taken showed 0.62 per cent of its oxide to be TiO_2 by the colorimetric determination, while the double fluoride of potassium and columbium obtained showed a TiO_2 content equal to 0.25 per cent of its oxide. Hence it would seem that by Method 1 the titanium or oxide with lower specific gravity and molecular weight did concentrate in the mother-liquors.

Crystals 2 and 3 (see *ante*) were combined. Their total weight was about 1 kilo. This, in portions of 100 grms. at a time, was dissolved in about 2 litres of water and fractionally precipitated with ammonium hydroxide, using dilute alkali and working in the cold with constant stirring. The alkali was added until the solution was barely acid to litmus; the precipitate formed was filtered off and the filtrate made alkaline with an excess of the precipitant. This second fraction contained about 3 to 4 grms. of oxide from each 100 grms. of double fluoride taken. These ten last fractions were combined and dissolved in hydrofluoric acid, 15 grms. of potassium hydroxide added, then dilute ammonium hydroxide until slightly acid, and the precipitate filtered out. It was marked A. Ammonium hydroxide was then added to the filtrate until litmus showed the reaction to be just neutral. The precipitate was designated B. C was obtained in the filtrate from B by adding a large excess of ammonium hydroxide. It (C) presumably should contain most of the titanium from the 1000 grms. of double fluoride taken. The oxide actually present in it was changed to double fluoride by dissolving in hydrofluoric acid and adding potassium carbonate. The first crop of crystals was obtained from strong hydrofluoric acid. It re-crystallised from the same in needles. These were analysed:—

0.6954 grm. of the sample gave 0.3018 grm. oxide and 0.3900 grm. potassium sulphate.

0.3018 : 0.3900 :: $x/2$: 174	$x = 269.3$.
Calculated, $\text{K}_2\text{C}_2\text{F}_7$.	Found.
Oxide 57.05	56.09
K_2SO_4 43.93	43.40

The specific gravity of the oxide equalled 4.45. 0.3 grm. of it showed the presence of the equivalent of 0.0025 grm. of TiO_2 , or 0.83 per cent.

The needles from C, not taken for analysis, and the mother-liquor were combined and evaporated to dryness on a water-bath to expel the excess of hydrofluoric acid. This was repeated once. The solution of the salt was then fractionally precipitated with ammonium hydroxide, the fractions up to the point where litmus showed a slightly alkaline reaction being discarded, when the filtrate from them was made strongly alkaline with ammonium hydroxide. The precipitate obtained was changed to its potassium double fluoride. About 2.5 grms. of the double salt were got.

Analysis.

0.7248 grm. of sample gave 0.3014 grm. of oxide and 0.4205 grm. of K_2SO_4 .

0.3014 : 0.4205 :: $x/2$: 174	$x = 249.4$.
Calculated, $\text{K}_2\text{C}_2\text{OF}_5\text{H}_2\text{O}$.	Found.
Oxide 57.81	58.02
K_2SO_4 44.52	41.58

The specific gravity of the oxide was found to be 4.667. 0.2930 grm. of oxide gave a colour with hydrogen peroxide equivalent to 0.0322 grm. of $\text{TiO}_2 = 11$ per cent.

The crucible in which the oxide was ignited was deeply stained. The analysis and the colour test showed the presence of titanium, while the stain on the crucible and the high specific gravity of the oxide could be due to tin in considerable amount, which is precipitated in the last fractions on fractional precipitation with ammonium hydroxide.

(To be continued).

Welfare Work.—The endeavours of Messrs. Burroughs, Wellcome, and Co. to promote the moral, mental, and physical betterment of their people has received recognition at the Liège International Exhibition just closed. A special Gold Medal was conferred upon them for the "Intellectual and Moral Development of Workers."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation, and published or passed for publication in the *Transactions*:

139. "Synthesis from Glucose of an Octamethylated Disaccharide. Methylation of Cane-sugar and of Maltose." By THOMAS PURDIE and JAMES COLQUHOUN IRVINE.

When a solution of tetramethyl glucose in pure benzene containing hydrogen chloride was heated at 105–115°, water was eliminated, and the rotatory power increased. The product, when distilled under reduced pressure, was a neutral dextrorotatory syrup without multirotation, which was devoid of action on Fehling's solution. The results of combustion and of methoxyl estimation agreed with the composition of an octamethylated disaccharide. Moreover, tetramethylglucose, which was recovered by heating the compound with dilute hydrochloric acid, appeared to be the sole product of the hydrolysis. These results indicate that condensation had occurred between two molecules of tetramethylglucose in the γ -oxide form, the product being an octamethyl glucosido-glucoside, which appears to be the first example of a synthesised disaccharide of the non-reducing type, represented by cane-sugar and trehalose.

140. "Studies in the Acridine Series. Part II. Action of Methyl Iodide on Benzoflavine." By JOHN THEODORE HEWITT and JOHN JACOB FOX.

The authors have extended their work on 2-amino-3:7-dimethylacridine (*Trans.*, 1904, lxxxv., 529) by an examination of benzoflavine (2:8-diamino-3:7-dimethyl-5-phenylacridine). Acetylation with acetic anhydride and fused sodium acetate has furnished a *diacetyl* and small quantities of a *tetracetyl* derivative.

Diacetylbenzoflavine gives a *methiodide*, $\text{C}_{26}\text{H}_{26}\text{O}_2\text{N}_3\text{I}$; ammonia acts on this giving a *base* $\text{C}_{24}\text{H}_{23}\text{ON}_3$, one molecule of acetic acid being removed in addition to hydriodic acid.

By complete hydrolysis (that is, a removal of both acetyl groups), salts are obtained of which the *sulphate*, $(\text{C}_{22}\text{H}_{21}\text{N}_3)_2\text{H}_2\text{SO}_4$, may be regarded as having a typical composition. The corresponding base does not contain oxygen, and since it lacks a carbinol hydroxyl its constitution must be regarded as para-quinonoid.

141. "Note on certain Derivatives of Cyclopropene." By DAVID TREVOR JONES.

The diethyl ester of methylcyclopropenedicarboxylic acid and the corresponding dimethyl ester both readily take up two atoms of bromine, ethyl dibromomethyltrimethylenedicarboxylate thus obtained being a liquid (b. p. 185/30° m.m.), whilst the dimethyl bromo-ester is a solid (m. p. 77°). When warmed with zinc and acetic acid, these additive products yielded the cyclopropene esters from which they were derived.

When ethyl dibromomethyltrimethylenedicarboxylate is condensed with two molecules of ethyl sodiomalonate, a non-volatile product is obtained, which, on saponification with potassium hydroxide, yields small quantities of a tribasic acid, $\text{C}_9\text{H}_9\text{O}_8$ (m. p. 222°).

The intermediate non-volatile product appears to contain ethyl methylcyclopropenetracarboxylate, the acid, $\text{C}_9\text{H}_9\text{O}_8$, owing its formation to the splitting of a linking by potassium hydroxide with subsequent lactone formation.

142. "Experiments on the Synthesis of the Terpenes. Part V. Derivatives of Ortho-cymene." By FRANCIS WILLIAM KAY and WILLIAM HENRY PERKIN, jun.

Terpenes belonging to the *o*-series have not previously been prepared, and the authors described a series of experiments by which many members of this group have been obtained.

143. "Experiments on the Synthesis of the Terpenes. Part VI. Derivatives of Meta-cymene." By WILLIAM HENRY PERKIN, jun., and GEORGE TATTERSALL.

The authors dealt with some hitherto unknown members of the *m*-series of terpenes which have been obtained from various derivatives of *m*-toluic acid with the aid of organo-magnesium compounds.

144. "Topic Axes and the Topic Parameters of the Alkali Sulphates and Selenates." By ALFRED EDWIN HOWARD TUTTON.

The conception of "topic axes," a combination of the crystallographical axes with the molecular volume, introduced independently by Muthmann in Germany and the author in this country, has proved of great value as an expression of the fundamental morphological structure of crystals. The author's surmise, published in 1894 (*Trans.*, lxxv., 659), as to the existence of relatively large interspaces between the structural units, has now been proved to be a fact by the results of the determinations of the topic axes of the ammonium salts.

The importance of correctly diagnosing the type of homogeneous structure present in a crystallised substance is emphasised, and the suggestion of Fedoroff (*Zeit. Kryst. Min.*, 1902, xxxv., 129), that the type present in the crystals of the alkali sulphates and selenates is a pseudo-hexagonal one, is taken up and shown to be probably in accordance with fact, although the symmetry is strictly rhombic; for the primary prism angle is less than 1° removed from 60° , and the crystals frequently show a pseudo-hexagonal habit and form pseudo-hexagonal triplets.

A new series of topic axes has therefore been calculated for these salts on the assumption of a pseudo-hexagonal space lattice, employing densities freshly determined with the aid of the suspension method for the calculation of the molecular volume involved. The results demonstrate even more elegantly the laws already published by the author, governing the relations of the morphological constants with the atomic weight of the alkali metal, and with that of the dominant negative element (sulphur or selenium) present, as also the rule regarding the position of ammonium near rubidium in the alkali series and the interesting corollary as to the existence of intermolecular and inter-atomic spaces.

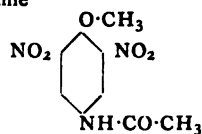
145. "The Relation of Position Isomerism to Optical Activity. IV. The Rotation of the Menthyl Esters of the Isomeric Nitrobenzoic Acids." By JULIUS BEREND COHEN and HENRY PERCY ARMES.

The previous observations on the effect of position isomerism on the rotation of menthyl benzoate have been confirmed. The *p*-nitro-group has the least, the *o*-nitro-group the greatest effect on the rotation, whilst the effect of the *m*-nitro-group lies between the two. The most striking difference in the effect of the nitro-group and that of the halogens previously studied (*Trans.*, 1903, lxxiii., 1213; 1904, lxxviii., 1262) is that, whereas the ortho-chlorine and -bromine diminish the amount of deviation, the *o*-nitro-group enormously increases it.

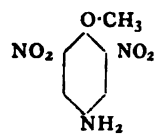
146. "Dinitroanisidines and their Products of Diazotisation." By RAPHAEL MELDOLA and FRANK GEORGE COAD STEPHENS.

This paper is in continuation of former work on the elimination of a nitro-group on diazotisation, and has been carried out in order to ascertain whether this elimination follows the ortho-para rule. The authors have found that when dinitro-*o*-anisidine is diazotised in presence of sulphuric acid and the product decomposed by heating with hydriodic acid, there is obtained a mixture of a new iododinitroanisole ($\text{C}_6\text{H}_4\text{OCH}_3\cdot\text{I}\cdot\text{NO}_2\cdot\text{NO}_2$ —1:2:4:5), melting at 146 — 147° , and the iododinitroresorcinol methyl ether (m. p. 115 — 116°) formerly described. This result shows that under the conditions of diazotisation specified there results a mixture of a diazonium salt and a quinone-diazide (diazo-oxide). By the nitration of the monacetyl derivative of *p*-aminophenol the authors have obtained, in accordance with the results recently published by Reverdin (*Arch. Sci.*

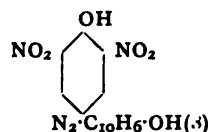
Phys. Nat., 1905, xix., 353), the acetyl derivative of the isopicramic acid ($\text{C}_6\text{H}_2\cdot\text{OH}\cdot\text{NO}_2\cdot\text{NH}_2\cdot\text{NO}_2$ —1:2:4:6) of Dabney (*Am. Chem. Journ.*, 1883, v., 33). On methylation, this acetyl derivative yields a new dinitroacetanilide which, on hydrolysis, gives a new dinitroanisidine



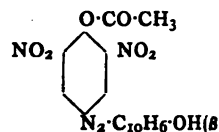
M. p. 157°
I.



M. p. 212°
II.



$\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\cdot)$
M. p. 269 — 270°
III.



$\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\delta)$
M. p. 259°
IV.

The latter on diazotisation does not lose a nitro-group, but the methyl of the methoxy-group is eliminated with the formation of the dinitroquinonediazide. The latter couples with β -naphthol in alkaline solution to form the azo-compound (III.), the acetyl derivative of the latter (IV.) being readily formed by heating the compound for a few minutes with acetic anhydride.

The authors have also prepared the dinitroacetanilide and dinitroanisidine corresponding to the new dinitroaminophenol recently described by Reverdin.

147. "Labile Isomerism among Benzoyl Derivatives of Salicylamide." By ARTHUR WALSH TITHERLEY and WILLIAM LONGTON HICKS.

A compound erroneously described by one of the authors (*Trans.*, 1902, lxxxi., 1533) as salicylbenzamide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, melting at 120° , which was obtained in the condensation of methylsalicylate and sodium benzamide, was shown to be a peculiar double compound of benzamide and salicylic acid, and *N*-benzoylsalicylamide has not yet been isolated. There are, however, two *o*-benzoyl derivatives of salicylamide, one melting at 208° , obtained in the above condensation, which is identical with the compound described by Gerhardt and Chiozza (*Ann. Chim. Phys.*, 1856, xlv., 139), the other (m. p. 144°) obtained by the authors by the wet benzoylation of salicylamide by benzoyl chloride in presence of sodium carbonate. Neither gives any colouration with ferric chloride, and there is strong evidence that in both compounds the benzoyl group is attached to phenolic oxygen. The more fusible isomeride is labile, and passes with remarkable ease into the other, the transformation in most cases being quantitative.

The change, however, is not reversible, and of the two it is the labile compound which must possess the ordinary amide structure, $\text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, since only the stable form, *o*-benzoylsalicyliminohydroxide, $\text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{NH}$, yields metallic salts.

Both forms on benzoylation in pyridine yield the same *O*-*N*-dibenzoylsalicylamide, $\text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHBz}$ (m. p. 129°), the stable substance giving a theoretical yield, the labile isomeride furnishing a much smaller proportion owing to simultaneous production of benzoylsalicylnitrile. There is evidence of the existence of two forms of the dibenzoyl derivative in equilibrium when the stable form melting at 129° is fused. On rapidly cooling, a brittle, amorphous glass is obtained which melts at 55 — 60° , solidifies again at 85° , and then melts at 128° .

148. "Preparation of Benzeneazocoumarin; its Bearing on the Constitution of *p* Hydroxyazo-compounds." By HERBERT VICTOR MITCHELL.

The existence, and extreme ease of formation, of

benzeneazocoumarin and the three nitrobenzeneazocoumarins favours the view that the *p*-hydroxyazo-compounds are really phenolic in character and not derivatives of quinonephenylhydrazone.

149. "*The Combustion of Acetylene.*" By WILLIAM ARTHUR BONE and GEORGE WILLIAM ANDREW.

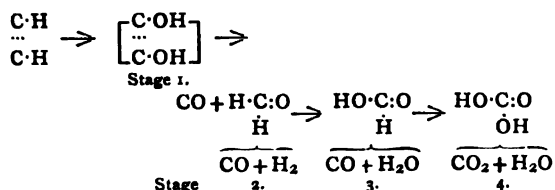
The authors' experiments proved that—

1. The combustion of acetylene does not involve the preferential oxidation of either carbon or hydrogen. Separation of carbon or hydrogen, when it does occur, must be entirely ascribed to secondary thermal decompositions.

2. Carbon monoxide and formaldehyde simultaneously arise at an early stage of the process, probably as the result of the decomposition of an unstable primary product

$\text{C}_2\text{H}_2\text{O}_2$, such as $\begin{array}{c} \text{C}\cdot\text{OH} \\ | \\ \text{C}\cdot\text{OH} \end{array}$. The formation of formaldehyde

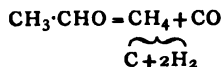
certainly precedes that of steam. The whole process may be represented by the following scheme :—



Below the ignition point, the formic and carbonic acids produced at Stages 3 and 4 respectively break down, forming steam and oxides of carbon, whilst above the ignition point the formaldehyde produced at Stage 2 (or possibly also the dihydroxyacetylene at Stage 1) is resolved into carbon monoxide and hydrogen. The explosive combustion may therefore be represented by the empirical equation $C_2H_2 + O_2 = 2CO + H_2$ (see Bone and Cain, *Trans.*, 1897, lxxi., 26).

3. Below the ignition point, excess of oxygen over and above an equimolecular proportion always retards the combustion. This was also shown to hold good above the ignition point by H. B. Dixon in his experiments on the rates of explosion of acetylene-oxygen mixtures (*Phil. Trans.*, 1893, clxxxiv., 183).

4. In contact with a hot catalysing surface, such as porous porcelain, acetylene unites with steam, forming acetaldehyde. This action may take place even in presence of oxygen, and introduces a complication whenever the hydrocarbon is being burnt over a hot surface. In such circumstances, the secondary decomposition of acetaldehyde might give rise to methane, or even carbon and hydrogen and carbon monoxide, thus:—



(Bone and Smith, *Trans.*, 1905, lxxxvii., 910).

5. Benzene is not produced in presence of oxygen below the ignition point.

150. "*Studies on the Origin of Colour-derivatives of Fluorene.*" By IDA SMEDLEY.

Experiments were made with the object of throwing further light on the question, under what conditions in ketonic compounds can halogens play the part of oxygen in contributing to the formation of coloured substances. The results supported the view that the power of the carbonyl group to act as a chromophore is destroyed by replacing the oxygen by two chlorine atoms; the effect of the other halogen atom requires further elucidation. Fluorenone chloride (m. p. 103°) was prepared and was found to be colourless, but attempts to replace the chlorine by iodine atoms were unsuccessful. Fluorenone, fluorenone chloride, and 9:9-dihydroxydiphenylfluorene (m. p. 223—224°) exhibit in a marked degree the property of "halo-

chromism" when dissolved in concentrated sulphuric acid. The action of alcoholic potassium hydrosulphide on fluorenone chloride produced a colourless disulphide (m. p. 161°); the similar action of alcoholic potassium sulphide did not form a thio-ketone, as was expected, but produced the red hydrocarbon, bisdiphenylene-ethylene and fluorenone.

151. "Note on the Zeisel Reaction in the case of Di-ortho-substituted Phenolic Ethers." By DAVID RUNCIMAN BOYD and JOHN EDMUND PITMAN.

Pyrogallol trimethyl ether is readily decomposed by aqueous hydriodic acid (sp. gr. 1.6), giving the theoretical yield of methyl iodide after heating for forty-five minutes.

Trichloroanisole and tribromoanisole, on the other hand, are left for the most part unaffected by such treatment. If, however, the solubility of these ethers is secured by employing, instead of aqueous hydriodic acid, a mixture of about equal volumes of hydriodic acid with glacial acetic acid, decomposition is complete after an hour's heating, and a theoretical yield of methyl iodide is obtained.

152. "*The Mechanism of the Hydrogen Sulphide Reduction of Nitro-compounds.*" By JULIUS BEREND COHEN and DOUGLAS McCANDLISH.

In the process of reducing different nitro-compounds with ammonium sulphide, or, as it is usually effected, with hydrogen sulphide in an alcoholic solution containing ammonia, great differences are noticeable in the rate of reduction, in the conditions under which reduction takes place, and in the nature of the products formed. From a study of upwards of forty different nitro-compounds, the authors have laid down the following empirical rule:—*The rate of reduction is increased by the presence of acidic (NO_2 , CO_2Me , Cl) groups and diminished by that of basic groups (CH_3 , NH_2), and is further affected by steric hindrance.* The authors show further that the reduction occurs in at least two well-defined steps, the first being attended by the formation of a hydroxylamine compound, which is easily identified by its property of liberating iodine from potassium iodide.

153. "*The Arylsulphonyl-p-diazoimides.*" By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

The new series of arylsulphonyl-*p*-diazotides (Trans., 1905, lxxvii., 74 and 921) has been extended by the preparation and investigation of *toluene-p*-sulphonyl-*p*-phenylenediazotide, 1:3-*xylylene-4*-sulphonyl-*p*-phenylenediazotide, and the more complex *benzene-1:3-disulphonylbis-p*-phenylenediazotide,—



A detailed examination of the first of these compounds showed that (1) the molecular complexity of the arylsulphonyl- β -diazomides corresponds with the simplest empirical formula for these substances; (2) cold mineral acids and even glacial acetic acid bring about a disruption of the β -diazomido-complex; (3) the β -diazomides readily yield azo-derivatives when condensed in an inert solvent with the phenols and the more reactive aromatic amines; and (4) when treated with caustic alkalis, preferably in alcoholic solution, the diazonitrogen of these diazomides is eliminated and replaced by hydrogen.

154. "The Reversibility of Photographic Development and the Retarding Action of Soluble Bromides." By SAMUEL EDWARD SHEPPARD.

It was shown experimentally that development is a reversible chemical reaction, and for ferrous oxalate the equilibrium factors were determined quantitatively. The retarding action of bromides enabled the parts played by diffusion and chemical action to be defined, and a general theory of development on this basis was brought forward.

155. "Studies in Chlorination. III. The Progressive Chlorination of Benzene in presence of the Aluminium-Mercury Couple." By JULIUS BEREND COHEN and PERCIVAL HARTLEY.

The conclusion is, therefore, that no compound is formed, and that this is a case of mutually soluble liquids of maximum vapour pressure. Cryoscopic determinations in benzene gave normal depression in the case of ethyl cyanide, but small values for alcohol and for the mixture of constant

boiling-point. Reasons are, however, given for attributing this in both cases, to reduction of osmotic pressure rather than to molecular association or combination.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 17, October 23, 1905.

Specific Heat of Copper Sulphate Solutions.—P. Vaillant.—The method employed by the author for the measurement of the specific heat of copper solutions is that of Joule, in which the metallic spiral which carries the current, and so heats the calorimeter, is replaced by the filament of an incandescent lamp. The substitution of the lamp for the spiral renders the method applicable to liquid conductors. As a result of a long series of experiments, the author finds that the specific heat of the dissolved sulphate rapidly increases with the concentration, and then seems to pass through a maximum. The variations can be explained by a triple influence:—1. The increase of molecular volume of the dissolved body with the dilution, which has the effect of diminishing the specific heat. 2. Electrolytic dissociation, which liberates the water of crystallisation, and has an effect similar to the above. 3. The transformation of the degree of hydration, $5H_2O$, to a state of inferior hydration which tends to diminish the specific heat at high concentrations. The specific heat of the molecule $CuSO_4 \cdot 5H_2O$, calculated by Kopp's law, is 0.2832.

Composition of the Hydrochloroferric Colloid.—G. Malfitano.—Using a 5 per cent solution of sublimed iron perchloride, which is heated to 100° or 115° for fifteen to thirty minutes, a colloid is obtained of which the composition has been represented by the formula $H_n(Fe_2O_6H_6)Cl$. On filtering through collodion the greater portion of this substance is retained; this latter substance the author designates as hydrochloroferric colloid. He investigates the composition of this material.

Certain Aromatic Oxides of Ethylene.—MM. Fournneau and Tiffeneau.—In a former paper the authors described a number of ethylene oxides, and noticed their greater or less aptitude for isomerisation into aldehydes or ketones under the influence of acids or heat. They now extend their researches to three series of aromatic ethylene oxides:—The mono-substituted oxides, $Ar-CH_2-\overset{\text{O}}{\underset{\text{O}}{\text{CH}}}-CH_2$; the di-substituted symmetric oxides, $Ar-\overset{\text{O}}{\underset{\text{O}}{\text{CH}}}-\overset{\text{O}}{\underset{\text{O}}{\text{CH}}}-CH_3$; and the di-substituted dissymmetric oxides, $Ar(CH_3)-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-CH_2$. They find that the former of these series of oxides are only partially isomerised under the influence of heat into the aldehydes $C_6H_5-CH_2-CHO$ and $Ar-CH_2-CH_2-CHO$. The second and third of these series, on the contrary, easily isomerise the former into arylketenes and the latter into the aldehydes $Ar-CH(CH_3)-CHO$. None of these isomerisms are accompanied by molecular migration.

MEETINGS FOR THE WEEK.

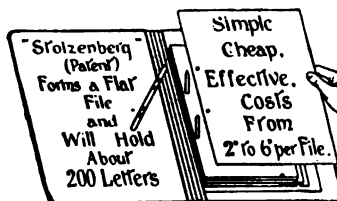
WEDNESDAY, 22nd.—Society of Arts, 8. "The Cinematograph and its Applications," by F. Martin-Duncan.

FRIDAY, 24th.—Physical, 5. "The Dielectric Strength of Air," by A. Russell. "Electrical Conductivity of Flames containing Salt Vapours for Rapidly Alternating Current," by H. A. Wilson. "Lateral Vibration of Loaded and Unloaded Bars," by J. Morrow.

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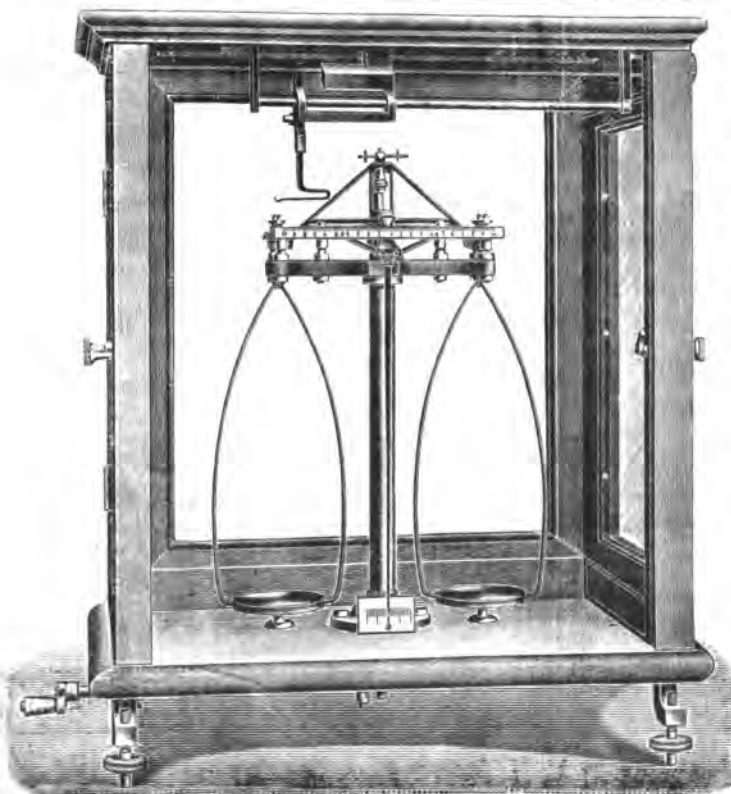
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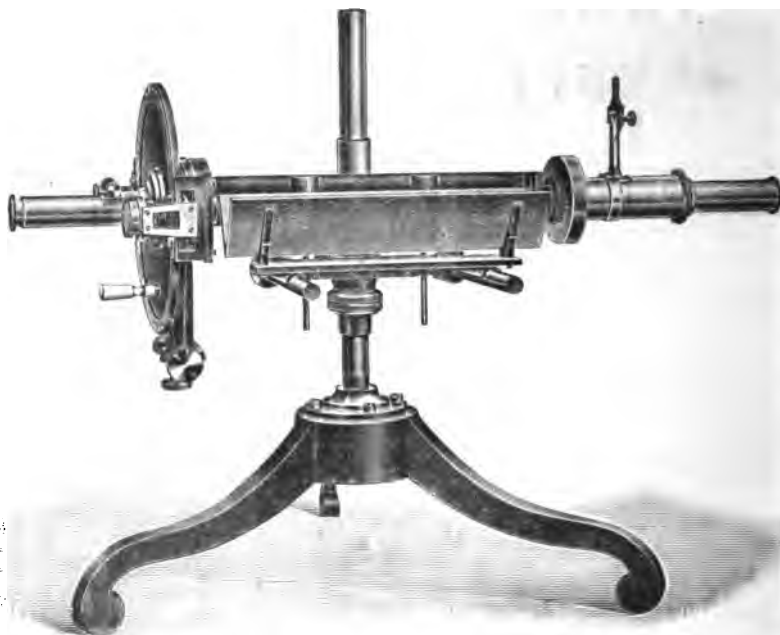
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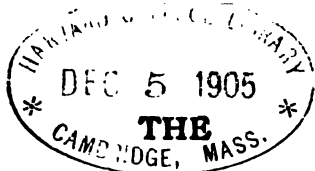
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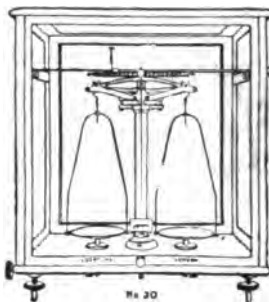
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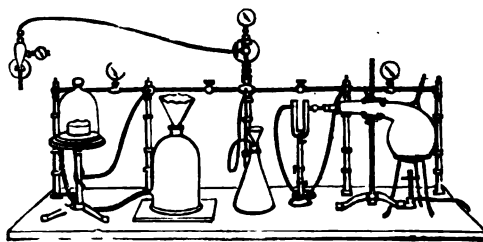
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THE CHEMICAL NEWS.

VOL. XCII., No. 2400.

THEORY OF PHOTOGRAPHIC PROCESSES.*

PART II.—ON THE CHEMICAL DYNAMICS OF DEVELOPMENT, INCLUDING THE MICROSCOPY OF THE IMAGE.

By S. E. SHEPPARD, B.Sc., and C. E. K. MEES, B.Sc.

(Concluded from p. 229).

Exposure through the Glass-side.

Two plates were given identical exposures behind the sector-wheel, and developed for ten minutes in N/10 ferrous oxalate at 15°. One was exposed through the glass-side; the other from film-side, but with a glass plate in front. On fixing, &c., although both showed five tones the densities of the glass-side plate were considerably less than that of the other. This agrees with Abegg (R. Abegg u. Cl. Immerwahr, *Sitz. ber. d. Wien. Akad.*, 1900, cxiv., abt. 2A) and Bellach (*loc. cit.*, p. 61).

Thickness of Negative Layer.

No.	Exposure.	Thickness (a).	D.	Thickness (b).	Db.
	C.M.S.	M.m.		M.m.	
1.	10	0.0204	—	0.0192	—
2.	5	0.0199	0.110	0.0180	0.257
3.	2.5	0.0188	0.042	0.0153	0.098
4.	1.25	0.0181	—	0.0152	0.027
5.	0.62	0.0148	—	0.0152	—

(a) Glass-side.

(b) Air-side.

The depth is much the same for both plates. According to Abegg, all the grains in back-exposed plate appeared equally developed, whereas Bellach describes his preparations as similar to front-exposed plates, *i.e.*, uppermost zone with few and small particles, mean characteristic layer, and lowest with very small particles. In our plates the appearance agreed with Abegg's description, the increase in size of grain being in the opposite sense to that of a film-side exposed plate. The apparent divergence in description is probably due to the fact that Bellach used short development, one hundred and ten seconds, with a strong developer, while Abegg used prolonged stand development, more comparable with the author's conditions. The result shows that, other things being equal, the grain receiving most exposure is most reactive and starts development first.

Thus, for 1.25 C.M.S. exposure,—

	Micro-diameter.	Focus.
	M.m.	Divs.
Film-side plate ..	{ 0.00135 0.0008	76.0 74.6
Glass-side plate..	{ 0.00106 0.00140	79.5 77.0

The number of grains was greater in the plate exposed from air-side. For 1 m.m.² of film,—

Air-side ..	132 × 10 ³
Glass-side ..	71 × 10 ³

while Abegg and Immerwahr give 41.0 × 10³ and

32.5 × 10³. Both the densities and the number of grains are greater for the air-side plate. Abegg attributes this to the prevention of halogen diffusion. Braun's observation on the part played by oxygen in the formation of latent images may also account for it, however (*Zeit. f. Wiss. Phot.*, vol. ii., Heft 8). Possibly connected with this is the statement of Th. Wulf that, for the so-called photo-electric effect, the sensitiveness to light increases as the potential fall of electrode to surrounding gas increases (*Ann der Phys.*, [4], ix., 946).

The general results of the microscopic survey are in agreement with the theory of development proposed before. Each grain develops as a more or less isolated system, only uniting to form "aggregates" with other grains at high exposures when the packing is closer. The thickness of the reaction-layer is from 0.02 to 0.04 m.m.—a value similar to that found by Brunner for many heterogeneous reactions. But in this case the solid phase lies entirely in the layer. The diffusion of the developer may be divided into two parts:—(a) Through the total thickness, δ ; (b) through the micro-layer, δ' , of the order 0.0005 m.m. surrounding the grain. This is the true reaction-layer, and the reaction is somewhat like to the catalysis of H₂O₂ by colloidal metals, save that there is no convection. As the diffusion has to take place through gelatine, the structure and state of this may influence the velocity. This will be dealt with later. The fact that the size of the grain with low time of development—or, better, low development-factor—varies with the exposure, indicates that the "reactivity" of the individual haloid grain is a steady function of the exposure. Hence at low development-factors departures from the law of constant density-ratios are possible, but difficult to confirm. Such departures will be the more marked whenever the chemical velocity approaches that of the diffusion process.

The conclusions given here were confirmed for other developers, and we hope to publish them later in connection with the general survey of these; since this work was finished, Messrs. Lumière (*Zeit. f. Wiss. Phot.*, ii., 256) and Wallace (*Astrophysical Journal*, 1905) have published short studies on the size of the grain. Their results do not contradict ours, but they do not seem to have considered sufficiently the effect of the degree of development, γ , on all observations.

The Early Stages of Development.—Considerable information concerning the velocity of development can be obtained from the "time of appearance" of the image, which is a function of it. In 1893 Mr. Watkins announced that for any given reducer the time of appearance gave an accurate indication of the speed of working, and that any variation in the alkali, temperature, or strength affected the time necessary to reach a given density or development-factor in the same proportion that it affected the time of appearance. Generally stated, $T_D = W T_A$; where T_D is time for density (D), T_A is time of appearance, and W is a constant.

This rule has been usefully applied in practice for timing development, but the above statement is too wide, both experiment and theory showing that such a simple relation does not hold for many complex developing solutions. The following considerations from the theory of the order of reactions explain both the rule and the deviations from it (Ostwald, "Lehrbuch," 2te Auflage, vol. ii., p. 236):—

If two analogous reactions continue to equal fractions of the total change, then the times necessary for this are inversely as the velocity factors.

Of course, it is assumed that the same function of the variables still represents the course of the reaction. If experiments with different concentrations are carried to the same fraction of these, the following relations hold:—For reactions of the first order the factors are directly, the times inversely as the concentrations, of the second order as the squares, and so on. We may apply this to development as follows:—The density which is first visible, *i.e.*, first distinction between exposed and unexposed, is a physiological constant and a fixed density, θ , say

* A Paper read before the Royal Society, March 30, 1905.

(Schwellenwerth).^{*} Hence for same exposure, i.e., same final density, θ is always an equal fraction of the total density; so θ , the time of appearance, i.e., for density, θ , is inversely as the velocity coefficient, and is similarly modified by concentration, &c.

With different final densities and constant developer, the values of θ are inversely as the final densities, D_1 , D_2 , &c. Here, of course, θ measures an equal fraction of the total oxidation of reducer.

Let D_1 and D_2 be any two final densities, and λ a fixed density, where D_1 , D_2 = or $>$ λ , and let θ_1 and θ_2 be their respective times of appearance, and t_1 , t_2 corresponding times to reach λ . Then we have—

$$t_1 \theta_1 = t_2 \theta_2 = t_n \theta_n = \text{constant } W,$$

whose numerical measure is proportional to the Watkins multiple, and is independent of concentration and only dependent on velocity function.

The general theorem is only true for simple reactions, and does not hold for "graded," "catalysed," and so forth. The same limitations hold for development, and the occurrence of initial disturbances, varying in the specific developers, probably account for the wide variation of the Watkins multiple for various developers, and also its variation with the same reducer. Only for developers in which the balance between reduction-potential and diffusivity is within certain limits will W be constant, since deviations will easily occur for such a small fraction of the total change, and yet the development-function remain much the same.

The writers have extensively developed the use of the "time of appearance" for investigation of development kinetics. The most similar use of such a method of inquiry in chemical dynamics is A. von Oettingen's research on the decomposition of thiosulphate by acids, in which the "time of appearance" of the sulphur cloud was observed (*Zeit. f. Phys. Chem.*, vol. xxx.; cf. also H. Landolt, *Ber.*, 1886, vol. xix., p. 1317). The limiting conditions for experimental accuracy discussed there hold also for development. The time must not be so short that the limiting error of measurement seriously affects the result, nor so long as to cause doubt as to the exact moment. The observations are made in a dark room, but using as much of a steady reddish light as possible, since subsequent fogging is in general immaterial.

The timing was done with a stop-watch marking one-fifth of a second; several observations of each time were made, and the mean used, and all measurements for comparison made at one period. The method is accurate within the limits employed to about 2 per cent.

Effect of Concentration with Ferrous Oxalate.

TABLE XI.—Plate, Wratten Ordinary, Exposed 8 C.M.M.

Concentration.	T_A in secs.	Mean T_A .	$C = \text{Product}$.
0.2 N.	22.0, 19.0, 19.0, 18.8	19.7	3.94
0.1 N.	40.4, 40.0, 40.2	40.1	4.01
0.05 N.	81.0, 79.8, 80.5	80.4	4.02
0.025 N.	160.2, 158.2, 157.0	158.4	3.96
Mean		39.8	

This shows from N/5 to N/40 the velocity is directly proportional to the concentration, even at this early stage of development.

Temperature and Development Velocity.

Experiment showed that the variation of temperature did not influence the density ratios. The effect of temperature

on the velocity constant, $K = \frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$, was measured,

^{*} This fact rests on the existence of a Schwellenwerth or "threshold" value of perception of contrast by the eye.

and also on $V = 1/T_A$. In this case four series of measurements were made, embracing the range 0° C. to 30° C. By interpolation the reduced results gave the following table:—

TABLE XII.—Developed in N/12.5 Ferrous Oxalate.

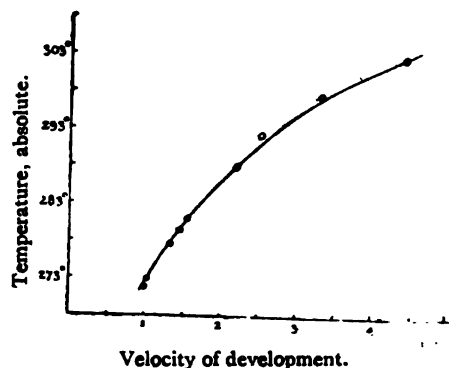
Temperature.	Absolute.	Velocity.	V. mean.
-0.8° C.	272.2	1.00	1.00
0.0	273.0	1.01	1.01
5.2	278.2	1.29	1.29
6.7	279.7	1.33	1.33
9.2	281.2	1.42, 1.56, 1.51	1.50
15.0	288.0	2.126	2.13
20.0	293.0	2.50	2.50
25.0	298.0	3.29	3.29
30.0	303.0	4.35	4.35

Van't Hoff's equation, $\frac{d \log K}{dT} = \frac{A}{T^2}$ (*Kgl. Svenska Vet. Hdl.*, 1885, vol. xxi., No. 17), in the integrated form for A sensibly constant, $\log K = -\frac{A}{T} + C$ was found to represent the results very fairly.

TABLE XIII.— C found as 7.60.

Temperature.	A.	V obs.	V calc.	Δ per cent.
272.0	1794	1.00	0.982	-1.8
273.0	1798	1.01	0.991	-1.9
278.2	1807	1.29	1.290	0.0
279.7	1911	1.33	1.380	+4.0
281.2	1806	1.50	1.506	+0.4
288.0	1806	2.13	2.133	+0.1
293.0	1817	2.50	2.69	+8.0
298.0	1813	3.29	3.467	+5.0
303.0	1807	4.35	4.361	+0.25

Curve calculated from $\log K = -1806/T + 7.60$.



CURVE II.

The temperature coefficient for 10° from 0° to 30° C. is $(K + 10^\circ)/K = 1.7$.

The validity of these results is shown by measurements of K , the mean velocity coefficient.

TABLE XIV.

Temperature.	K found.	K calc.	Δ per cent.
9.6° C.	0.0632	0.0632	—
20.8	0.0870	0.0891	+2.2
30.7	0.1174	0.1210	+2.0

The Temperature Coefficient.

Bodenstein (*Zeit. Phys. Chem.*, 1904, vol. xlix., p. 42) and Senter (*Proc. Roy. Soc.*, vol. lxxiv., 214) have indicated the value of the temperature coefficient for 10° as a criterion in heterogeneous reactions. For chemical reactions in homogeneous solution the value is generally about 2 to 3 (van 't Hoff, "Vorlesungen," vol. i., p. 225), while Brunner found 1.5 for rate of solution of benzoic acid in water; for diffusion processes we should expect a value about 1.5, and not varying for different bodies very much.

Now we have found that the expression—

$$K = \frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$$

can be used to measure the development velocity for most developers. A preliminary study of the temperature coefficient for different emulsions and developers gave the following results:—

TABLE XV.

Reducer.	Emulsion A.	B.	C.
Fe(C ₂ O ₄)	1.60	1.90	1.70
FeF	1.52	—	—
Fe citrate	1.54	—	—
C ₆ H ₄ (OH) ₂ p. ..	—	2.10	—
C ₆ H ₄ (OH) ₂ o. ..	—	2.80	—

The temperature coefficient frequently passes the value to be expected from the diffusion theory. But in the case of development, we must be cautious in applying the criterion, as the following consideration will show:—

Beside the increase in diffusivity (mobility of reducing molecule), we must also consider—(a) Alteration of resistance to diffusion in gelatin; (b) in complex developing solutions, alteration of concentration of reducing ion by changing the chemical equilibrium, especially in alkaline developers. Under these conditions a high temperature coefficient in development does not necessarily mean that the velocity is that of a chemical reaction.

In the case of ferrous oxalate, the theoretical formula of van 't Hoff, which is a deduction from the reaction isochore, was employed. This is not legitimate in the case of diffusion phenomena, and the best formulation would probably be the ordinary parabolic interpolation formula in the form $K_t = K_0(1 + at + bt^2)$; a comparison of the constants a and b for different plates and developers should yield useful information on temperature influences.

Resistance of the Gelatin.

Hardening agents, which raise the melting-point of the gelatin, are generally supposed to alter the velocity of development by changing the diffusivity. Many emulsions, however, show no such effect. Thus, with formalin (40 per cent formaldehyde) in 4 per cent strength and increasing time of immersion, although the film became quite insoluble in boiling water, the development velocity was not lowered.

TABLE XVI.

No.	Time of immersion. Secs.	T _a in secs.	Mean. Secs.
1.	0	24.0, 23.2, 24.0	23.7
2.	30	24.0, 24.2, 23.8	24.0
3.	60	24.0, 24.2, 23.4	23.9
4.	120	23.6, 24.6, 24.0	24.0
5.	240	24.0, 23.0, 23.4	23.4
6.	8 per cent, 10 mins.	25.2, 23.4	24.3

$$T = 23.9$$

The general theory of the action of hardening agents will be discussed later in connection with the destruction of the "latent image."

"Penetration" of Developer.

By the rate of penetration the time for the reducer to pass through the reaction-layer, δ , is understood. This was studied as follows:—

If plates are exposed through the glass-side, the image will lie nearer the glass, and we may expect it to appear—

a. On front first if the penetration of the developer count most.

b. On back first if the greater reactivity of the more exposed particles be the predominant factor.

A strip of Ilford ordinary film was exposed, cut up, and developed in N/10 ferrous oxalate at 15° C.

The values of T_a given are means of four experiments.

TABLE XVII.

Exposure.	T _a film-side.	T _a glass-side.
Ilford film—300 C.M.S.	40.3 secs.	45.3 secs.
60 "	54.6 "	52.6 "
10 "	72.4 "	63.0 "
Wratten ordinary—300 C.M.S. ..	94.2 "	90.4 "

Consequently, with low exposures, the back appears before the front, but as the exposure increases, the developer being the same, the two times become equal, and eventually the image appears on front first. This was confirmed on plates exposed in the sensitometer.

Plates given the same exposure from the front always show the image from the front first, the relative difference in time being somewhat greater, the absolute value of T_a always less.

The above phenomena may be explained by the following considerations drawn from the microscopy of the image:—

a. The absolute thickness of the layer of developable particles increases but slightly with the exposure.

b. Reckoning down through the layer from the exposed side, the reactivity of each layer of grains diminishes through the thickness. The slope of this reactivity-gradient then depends upon the exposure.

c. With short time of development the penetration increases rapidly; further, as the developer reaches the lowest layers, its concentration will be diminished somewhat by diffusion and oxidation by developable AgBr. There will therefore be a concentration gradient through the film.

d. Then in the case of exposure from air-side, the two gradients will be in the same direction, and will reinforce each other; for exposure from the back, the gradients will be opposite in sense, and the front layers or back will appear first according as one factor or the other predominates.

This result is in agreement with the microscopic deduction, that, other things being equal, the more exposed grains possess the greater reactivity and start developing first.

With regard to the absolute time required for the developer to penetrate the thickness of the film, an estimate can be obtained as follows:—With an Ilford film, the γ, t curve of which was known, the least time of appearance at the back for any exposure through the back was about ten seconds with N/10 ferrous oxalate at 15° C. Now, under these conditions, the half-period of development, i.e., for $\gamma_{\infty}/2$, was 5.0 minutes. Hence the error due to incomplete penetration is not of a very large order, and, moreover, reasons will be given later for assuming a chemical-induction generally greater than any diffusion-induction. However, for accurate comparison of velocities, in order to avoid an erroneous time-zero, the form—

$$K = \frac{1}{t_2 - t_1} \log \frac{\gamma_{\infty} - \gamma_1}{\gamma_{\infty} - \gamma_2}$$

is the most suitable (Senter, *loc. cit.*, p. 203; see also Ostwald-Luther, "Physico-chem. Messungen," p. 455).

In development the temperature-coefficient has been found an inadequate criterion for distinguishing diffusion

from chemical velocity. Such a criterion, however, we believe to exist in the action of soluble bromides, and in a discussion of this and the reversibility of development we hope to show that the development process probably takes place in general in two phases, in the first period the chemical velocity being slow compared with diffusion, in the second the contrary holding. It is the velocity of the second period which is usually measured.

In conclusion, we have much pleasure in expressing our great thanks to Sir William Ramsay, F.R.S., for his interest in the investigation.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

(Continued from p. 233).

THE crystals and the mother-liquor remaining from this salt were dissolved in boiling water and an excess of sodium hydrate added, when a heavy flocculent precipitate separated. This was filtered, boiled with water, and the insoluble portion changed to double fluoride. It was again taken up in boiling water, and an excess of sodium hydroxide added. The precipitation was not complete. The portion precipitated was treated with boiling water, filtered, and the filtrate found to contain a large amount of titanium. That portion of the precipitate insoluble in water was changed to double fluoride.

Analysis.

0.5570 grm. of sample gave 0.2248 grm. of oxide and 0.3468 grm. of K_2SO_4 .

0.2248 : 0.3468 :: $x/2$: 174 $x = 225.6$.

The sp. gr. of the oxide was found to be 4.2. The oxide gave a colour with hydrogen peroxide showing the presence of about 21 per cent TiO_2 .

Crystals "A" were changed to double fluoride and re-crystallised.

Analysis.

0.7184 grm. of sample gave 0.3188 grm. of oxide and 0.4176 grm. of potassium sulphate.

0.3188 : 0.4176 :: $x/2$: 174 $x = 265.7$.

Calculated, $K_2C_2O_7 \cdot H_2O$. Found.

Oxide	44.52	44.38
K_2SO_4	57.81	58.13

The sp. gr. of the oxide was found to be 4.481. 0.3160 grm. of oxide gave a colour with hydrogen peroxide equivalent to 0.0022 grm. $TiO_2 = 0.7$ per cent.

Crystals "B" analysed as follows:—

0.8098 grm. of sample gave 0.3614 grm. of oxide and 0.4708 grm. of K_2SO_4 .

0.3614 : 0.4708 :: $x/2$: 174 $x = 267.0$.

Calculated, $K_2C_2O_7 \cdot H_2O$. Found.

Oxide	44.52	44.63
K_2SO_4	57.81	58.14

The sp. gr. of the oxide was found to be 4.864. 0.3600 grm. of oxide gave with hydrogen peroxide a colour equivalent to 0.0013 grm. of $TiO_2 = 0.36$ per cent.

Having failed to get any evidence of the existence of neptunium in the last fractions of the double fluoride from the South Dakota mineral, it was decided to test some of the mineral from Haddam, Conn., the source of the material used by Hermann in his investigation. The last fractions of the potassium double fluoride from 5.87 kilos. of columbite from Haddam, Conn., amounting to 100 grms., were dissolved in boiling water, and an excess of sodium hydroxide added. The precipitate obtained was partly crystalline

and partly flocculent, as described by Hermann. It was filtered out, dried on a porous plate, and boiled with 25 parts of water. The crystals dissolved, leaving a yellowish residue evidently containing much iron. This residue gave a yellow coloured bead in the reducing flame containing so much iron that it was impossible with a small blowpipe to keep it all reduced. Is it not probable that this is what Hermann supposed was neptunium?

This salt was fused with acid potassium sulphate to remove the iron, the oxide remaining after extracting the fusion with boiling water was changed to double fluoride, dissolved in boiling water, and an excess of sodium hydroxide added. The precipitate obtained was crystalline and perfectly soluble in water, leaving an inappreciable residue. From all of which it may be inferred that the material from the Haddam locality showed no more evidence of neptunium than did that from South Dakota.

Ten kilograms of the main bulk of the potassium columbium oxyfluoride were crystallised from strong hydrofluoric acid. Five hundred grms. were taken at one time, and the mother-liquors from the two fractions combined, evaporated one-half, and another crop of crystals removed. The mother-liquors from these were united and evaporated, the crystals obtained were re-crystallised, the mother-liquors from the re-crystallisation combined and evaporated to dryness with sulphuric acid. The oxide obtained from that portion evaporated to dryness was 5 grms. The fraction of crystals immediately preceding, 60 grms. in weight, was decomposed with sulphuric acid and the oxide obtained from it. The 5 grms. of oxide and about one-half of the oxide from the 60 grms. of double fluoride were heated in carbon tetrachloride vapours, taking about 2 grms. of oxide at a time. The more volatile portion, which should contain the most of the $TiCl_4$, was distilled away from the $CbOCl_3$. The portions of this liquid were combined, the oxides—3 grms.—obtained from it, and these oxides again heated in CCl_4 . Again, only the liquid portion and that of the solid which was carried over mechanically was taken. The oxide from this portion was changed to double fluoride.

Analysis.

0.5678 grm. of sample contained 0.2196 grm. of oxide and 0.3390 grm. of K_2SO_4 .

0.2196 : 0.3390 :: $x/2$: 174 $x = 225.4$.

Calculated, $K_2C_2O_7 \cdot H_2O$. Found.

Oxide	44.52	38.6
K_2SO_4	57.81	59.7

Amount of TiO_2 in the oxide 0.0594 grm. = 29.7 per cent.

The oxide from the salt taken for analysis was combined with the oxide from the double fluoride not taken for analysis, and this with the remaining half of the oxide from the 60 grms. of double fluoride mentioned above was mixed with the oxide from all the previous double fluorides which had been tested for titanium and shown its presence in a fair degree. This mixture of oxides was heated in a current of sulphur monochloride, the chloride formed collected in a receiver, and this was then heated until all of the sulphur monochloride was distilled out. This sulphur monochloride and any other chlorides which it might contain was again distilled to remove the last of the columbium chloride which might have been carried over mechanically. It was then treated with water and oxalic acid, the sulphur filtered off, and any oxide dissolved in the oxalic acid precipitated with ammonium hydroxide. This hydrate was changed to potassium double fluoride.

Analysis.

0.5444 grm. of sample gave 0.1952 grm. of oxide and 0.3850 grm. of potassium sulphate.

0.1952 : 0.3850 :: $x/2$: 174 $x = 175.9$.

Calculated, $K_2C_2O_7 \cdot H_2O$. Found.

Oxide	44.52	33.33	35.85
K_2SO_4	57.81	72.50	70.72

* Proceeding* of the American Philosophical Society, 1905, xlv., p. 177.

0.0310 grm. of the oxide was found to contain 0.244 grm. TiO_2 , or 78.7 per cent.

A solution of the oxide in hydrochloric acid reduced with zinc to an amethyst or violet colour; the oxide also gave a violet titanium bead in the reducing flame with salt of phosphorus.

It would seem that about 80 per cent of the oxide from this double fluoride was TiO_2 .

The remainder of the double fluoride, about 0.5 grm., was dissolved in the mother-liquor from which it came by heating, and an excess of sodium hydrate added. A flocculent precipitate formed. After cooling, this was filtered off, and the filtrate acidified with hydrochloric acid, and tested for metallic acids with ammonium hydroxide. A precipitate was obtained, which was filtered out, and, after washing thoroughly, dissolved in hydrochloric acid.

Upon passing hydrogen sulphide through this solution a heavy precipitate of yellow stannic sulphide was obtained, showing that tin had been carried over with the titanium by the sulphur monochloride.

The precipitate formed by the excess of sodium hydroxide was drained thoroughly and boiled up with water. Nothing went into solution as would have happened had there been any sodium columbate in the precipitate. This well washed precipitate was dissolved in hydrofluoric acid and potassium carbonate added to change it to the potassium double fluoride.

Analysis of the Crystals obtained.

0.1893 grm. of sample gave 0.0642 grm. of TiO_2 and 0.1366 grm. of K_2SO_4 .

	Calculated.	Found.
Oxide . . .	33.33	33.91
K_2SO_4 . . .	72.50	72.16

The determination of the TiO_2 colorimetrically gave 0.0636 grm. The salt was undoubtedly potassium-titanium fluoride, proving conclusively the presence of titanium in columbite.

(To be continued).

PROCEEDINGS OF SOCIETIES.

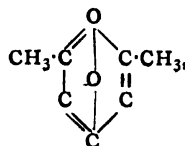
CHEMICAL SOCIETY.

The following complete the abstracts of papers received during the vacation, and published or passed for publication in the *Transactions* :—

161. "Molecular Refractions of Dimethylpyrone and its Allies, and the Quadrivalency of Oxygen." By IDA FRANCES HOMFRAY.

In most cases of associated compounds containing oxygen, the quadrivalency of that element is probable, and the observed molecular refractions are always in excess of those derived from the additive constants. The inference is that the atomic refraction of quadrivalent oxygen is greater than the highest of the values for the bivalent atom. No satisfactory data have been published for the determination of this constant, and the compounds which appear to afford the best opportunity for such investigation are dimethylpyrone and its allies and derivatives. Accordingly, the molecular refractions of the following easily purified substances have been determined, and all data are given. Dimethylpyrone and its hydrochloride, the compound of dimethylpyrone and alcohol, diacetylacetone, pyrone, and its hydrochloride, pyromeconic acid, ethyl chelidonate, ethyl xanthochelidonate, and dehydracetic acid. Measurements were made in solution in various solvents, the specific refraction of the solute being deduced in the usual way. The possible error is estimated at about 1 per cent. When the usual formulæ, not involving quadrivalent oxygen, are used, the calculated molecular re-

fractions are in all cases considerably too low. The modified formula for dimethylpyrone proposed by Professor Collie is—



and all the other compounds examined here may be expressed by analogous formulæ. The atomic refraction of quadrivalent oxygen for the D-spectral line required by these formulæ to satisfy the experimental numbers has been found by subtraction in each case, and a good agreement between these values is obtained, the mean being 2.73.

The molecular refractions re-calculated with this number for quadrivalent oxygen agree in most cases with the experimental to within the limit of accuracy of measurement.

162. "The Alkylation of Mannose." By JAMES COLQUHOUN IRVINE and AGNES MARION MOODIE.

α -Methylmannoside has been alkylated in methyl-alcoholic solution by means of silver oxide and methyl iodide with the production of a crystalline tetramethyl α -methylmannoside, and this compound, when hydrolysed by means of dilute hydrochloric acid, was converted into tetramethyl mannose.

The alkylated sugar proved to be a colourless syrup, and when heated with methyl alcohol containing 0.25 per cent hydrochloric acid it behaved like mannose, producing only the α -modification of the corresponding mannoside. Consequently the crystalline tetramethyl α -methylmannoside was the sole product of the reaction. When the alkylation was effected by means of silver oxide and methyl iodide, however, a different result was obtained. The product was a colourless, laevorotatory liquid, and this was shown to consist of a mixture of the α - and β -modifications of the fully methylated methylmannoside. The β -isomeride differs from the α -form in its laevorotation and in its ready hydrolysis by means of dilute hydrochloric acid or by the action of emulsin.

163. "The Interaction of Acridines with Magnesium Alkyl Halides." By ALFRED SENIER, PERCY CORLETT AUSTEN, and ROSALIND CLARKE.

By the application of Grignard's reaction to acridine and its homologues, a series of coloured crystalline compounds has been obtained. Endeavours to replace the metal magnesium by calcium were, however, unsuccessful, for in attempting to prepare calcium alkyl and aryl halides a change resembling Fittig's reaction always occurred almost exclusively (compare Beckmann, *Ber.*, 1905, xxxviii., 904). The magnesium compounds, although readily formed, were very difficult to obtain in a pure state on account of their insolubility in inert solvents, and they were decomposed by glacial acetic acid, alcohol, and chloroform, the alcoholic solution yielding the original acridine.

On employing as solvents for the reagents ethers of high boiling-points, such as anisole and phenetole, or mixtures of either of these with ordinary ether, compounds of definite composition slowly crystallised. These products, which frequently change in colour on drying, retain variable proportions of ether, but this can be entirely removed by drying at 110–115°.

Most of the compounds examined were of the type of the diacridine hexahalides previously described (*Trans.*, 1904, lxxxv., 1199), and consist of two molecules of the base united with three molecules of the "reagent." In the case of hexamethylacridine, however, the type is that of the tetrahalides, one molecule of base combining with two of the "reagent."

164. "New Method of Determining Molecular Weights." By PHILIP BLACKMAN.

Isotonic solutions of different substances in the same

solvent having equal vapour pressures, it follows that if two solutions connected by vapour be allowed to attain equilibrium, their final volumes (v_1, v_2) will be inversely proportional to the number of dissolved molecules. This state of equilibrium is represented by the equation—

$$\frac{m_1}{m_2} = \frac{w_1}{w_2} \frac{v_2}{v_1}$$

(where m_1, m_2 , are the molecular weights of the substances, the weights, w_1, w_2 , of which are dissolved in the volumes, v_1, v_2 , of the same solvent.)

The apparatus consists of two graduated test-tubes connected by a T-piece, with a bulb in each of the limbs of the U-piece. The substances are introduced into the test-tubes, the solvent added, and the solutions boiled. After a time, several readings of the volumes (v_1, v_2) are taken and the molecular weight calculated from the foregoing equations. With careful boiling, good results can be obtained in remarkably short times.

165. "*Benzylphenylallylmethylammonium Compounds. A Complete Series of Four Optically Active Salts.*" By ALFRED WILLIAM HARVEY.

1-Benzylphenylallylmethylammonium 1-camphorsulphonate has been prepared, having a molecular rotatory power of an equal arithmetical value to that of its dextro-isomeride, and a series of salts of the optically active base combined with optically active camphorsulphonic acids have been obtained of the type:—



The method of effecting the resolution of the iodide of the externally compensated base has been somewhat modified, whereby the difficulties previously experienced have been obviated (compare *Trans.*, 1899, lxxv., 1127, and 1901, lxxix., 828).

166. "*Solid Solutions.*" By REINHOLD FREDERICK KORTE.

Experiments were made to determine whether barium sulphate precipitated in presence of a ferric salt forms a solid solution of ferric iron, or whether a ferrisulphate of barium is produced. The results showed that the amount of iron carried down with the barium sulphate does not increase in weight above a very small amount (about 1.3 per cent), however much of the ferric salt be present; also that there is a loss on ignition, implying the decomposition of an iron sulphate. Probably the point of saturation of barium sulphate with ferric iron is one in which the latter is present to only a minute extent, and it is also not impossible that the state of the ferric salt is that of a ferric sulphate.

The precipitation of calcium as oxalate in presence of salts of magnesium was next examined. Here, when the proportion of magnesium to calcium oxide exceeds 36MgO to 5CaO, a sudden rise in the proportion of magnesium to calcium takes place, from about 4.7 to 13.7 per cent. The magnesium is evidently present in the state of solid solution, and, although magnesium oxalate is an easily soluble salt, yet it cannot be removed from the calcium oxalate precipitate by washing.

In precipitating ferric hydroxide with ammonia in presence of a manganous salt, saturation of the ferric hydroxide with manganese takes place, when the proportion between Fe_2O_3 and MnO in solution is 5:1. A larger proportion of manganese in solution produces no change in the amount retained by the ferric precipitate, namely, 2 per cent. The absorption of small amounts of manganese by iron is nearly complete, being as much as 95 per cent. From this it follows that on re-dissolving and re-precipitating a ferric precipitate containing only a small proportion of manganese, little change in its composition takes place.

Ferric hydroxide also dissolves nickelous oxide, and a saturated solution is produced when the proportion between Fe_2O_3 and NiO in solution is 5.9 to 1.

Although manganous and nickel oxides are carried down with aluminium hydroxide, no regularity could be

observed; solid solution appears not to take place, but merely mechanical absorption by the gelatinous alumina.

Lead sulphate, precipitated in presence of other salts, does not carry down any metals in solid solution.

167. "*The Bromo-derivatives of Camphopyric Acid.*" By JOHN ADDYMAN GARDNER.

When *cis*-camphopyric acid is treated with bromine in the presence of phosphorus pentachloride and the mixture poured into water, the chief products are *cis*-bromocamphopyric acid and *cis*-bromocamphopyric anhydride, a small quantity of *trans*-bromocamphopyric acid being also formed.

If, however, camphopyric anhydride is used instead of camphopyric acid, the chief products are *trans*-bromocamphopyric acid and bromocamphopyric anhydride, little or no *cis*-bromocamphopyric acid being produced.

trans-Camphopyric acid, treated in a similar way, using phosphorus trichloride instead of pentachloride, yields mainly *cis*-bromocamphopyric acid, a little anhydride, but no *trans*-bromo-acid.

The *cis*-acid is readily convertible into its anhydride by the action of acetyl chloride, but the *trans*-acid is not affected by this reagent. On the other hand, *cis*-bromocamphopyric anhydride, on boiling with water is converted into a mixture of *trans*-bromocamphopyric acid and decomposition products, probably of the *cis*-acid.

The bromine atom is readily replaceable. By the action of nascent hydrogen, *trans*-bromocamphopyric acid yields *trans*-camphopyric acid, whilst both *cis*-bromocamphopyric acid and *cis*-bromocamphopyric anhydride give ordinary camphopyric acid. Under the influence of alkalis, the bromine atom in both acids may be replaced by hydroxyl.

168. "*The Reduction of Metallic Oxides by Aluminium Carbide.*" By JOHN NORMAN PRING.

Alloys of aluminium can be prepared by direct reduction of the oxide by carbon in presence of many other metals, whereas without such auxiliary metals the product consists chiefly of aluminium carbide. These considerations led to a detailed study of the reactions between aluminium carbide and metallic oxides and metals. It was found that the carbide behaves as a strong reducing agent. Up to 1400°, both the aluminium and the carbon are simultaneously oxidised, forming alumina, carbon dioxide, and the metal of the oxide. At higher temperatures, however, selective reduction becomes apparent, the reduction being more and more brought about by the carbon of the carbide the higher the temperature of reaction, the result being that alloys of aluminium and the reduced metal are obtained, the percentage of aluminium increasing with the temperature, and, in the case of iron, finally reaching the limit demanded by the equation $Fe_2O_3 + Al_4C_3 = 2Fe.4Al + 3CO$.

Calcium carbide was found to exhibit a similar behaviour, but to a less marked degree, interaction between lead oxide and excess of molten calcium carbide giving an alloy containing 2.6 per cent of calcium.

Aluminium carbide reacts with metals at temperatures above the melting-point of platinum to form aluminium alloys with liberation of free carbon; at higher temperatures, the reaction takes place with violence, and is complete.

A study of the action of metallic calcium on aluminium carbide showed that calcium carbide is formed at all temperatures above the melting-point of platinum, and as aluminium acts on calcium carbide, producing aluminium carbide, the reaction is probably reversible.

169. "*The Rusting of Iron.*" By WYNDHAM ROWLAND DUNSTAN, HOOPER ALBERT DICKINSON JOWETT, and ERNEST GOULDING.

A detailed account is given of the investigation on the rusting of iron, an outline of which has been already published (Dunstan, *Proc.*, 1903, xix., 150).

170. "*Studies in Comparative Cryoscopy. Part III. The Esters in Phenol Solution.*" By PHILIP WILFRED ROBERTSON.

The molecular depressions of the esters in phenol solu-

tion tend to increase with the concentration. In many instances, however, there is an initial association; that is, the molecular depression first decreases, so that under these conditions a minimum is exhibited in the molecular depression curve.

The concentration at which the minimum occurs is a characteristic for each ester, but is greater in the case of esters of high molecular weight. The initial association of these compounds becomes more rapid as the molecular weight increases.

The ethyl esters of the normal fatty acids differ from odd to even members of the series, but each division forms a perfectly definite series. Thus, in the case of the compounds with an even number of carbon atoms, the initial molecular depression reaches a maximum at the sixth member, falls to a minimum at the twelfth, and then rises to a second maximum when the chain contains sixteen carbon atoms.

The esters derived from polybasic acids are characterised by the following behaviour.

1. Their molecular depressions increase rapidly with the concentration.

2. The minimum in the molecular depression curve is not always exhibited.

3. They have extremely high initial molecular depressions.

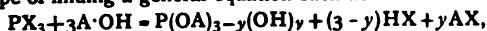
The negative "rate" of association and the abnormally high molecular depressions of the esters are probably due to the great tendency of phenol to form molecular complexes, since, in the case of the substituted phenols, thymol, guaiacol, and *o*-nitrophenol, which are not so strongly associated, these irregularities tend to disappear.

171. "The Iodides of Copper." By JAMES WALLACE WALKER and MARY VIOLETTE DOVER.

When equivalent solutions of potassium iodide and copper sulphate are mixed, the resulting precipitate seems to contain a definite polyiodide of copper mixed with the cuprous iodide, and not, as has been hitherto assumed, free iodine. Treatment of this precipitate with water gives a deep red solution, the analyses of which point to the formula CuI_4 for the solid polyiodide. From a study of the equilibrium between this solution and cuprous iodide, the authors conclude that it contains an equimolecular mixture of CuI_2 and CuI_6 . The limit of concentration of pure cupric iodide solution is almost exactly 0.1 per cent, removal of the water even in the form of ice inducing the reaction $6\text{CuI}_2 \rightleftharpoons \text{CuI}_6 + 5\text{CuI}$. Even higher polyiodides than this can be obtained from alcoholic solution.

172. "The Interaction of Alcohols and Phosphorous Halides." By JAMES WALLACE WALKER and FREDERICK MURRAY GODSCHALL JOHNSON.

The authors have studied the yield of alkyl halide obtained in the action of phosphorous chloride, bromide, and iodide on methyl, ethyl, and *n*-propyl alcohols, in the hope of finding a general equation such as—



applicable to the several cases. In this equation, X represents a halogen atom and A an alkyl group. In the production of methyl and *n*-propyl bromides, and of ethyl iodide, the value of *y* is 2; in the case of ethyl chloride, it is 1. In the other instances, the above equation would require to be doubled to express the results. The high degree of solubility of yellow phosphorus in methyl iodide suggested a ready method for the production of that substance in quantity. The theoretical weight of iodine is added to a 10 per cent solution of phosphorus in methyl iodide, and the equivalent amount of alcohol is slowly introduced. Enough phosphorus is then dissolved in the resultant liquid to produce again a 10 per cent solution, and iodine and alcohol are added as before. By continuing this process a large quantity of methyl iodide may be obtained in a short time, the yield being 94 per cent of the theoretical. Only 65 per cent of the theoretical yield of ethyl iodide was obtained by this method. Instead of employing the phosphorus and iodine in the ratio required

for the production of the tri-iodide, an almost equally good result is obtained by adding enough iodine to produce the penta-iodide, this compound being much more soluble than the tri-iodide in methyl iodide.

173. "The Electrical Conductivities of some Salt Solutions in Acetamide." By JAMES WALLACE WALKER and FREDERICK MURRAY GODSCHALL JOHNSON.

The salts examined were mercuric chloride, potassium chloride, iodide, and cyanide. Of these the first is the only normal electrolyte, the others showing a maximum of molecular conductivity at about 30 or 40 litres, which then falls to about half value on dilution. Mercuric chloride is known to give a compound with acetamide, and potassium iodide is found to yield the compound $\text{KI}\cdot 6\text{CH}_3\cdot\text{CO}\cdot\text{NH}_2$. The migration ratio of the iodion is found to be greater than in aqueous solution, a fact which points to combination of the ions with the solvent.

174. "Contributions to Our Knowledge of the Aconite Alkaloids. Part XVI. Indaconitine, the Alkaloid of *Aconitum chasmanthum*." By WYNDHAM ROWLAND DUNSTAN and ALBERT EDWARD ANDREWS.

Indaconitine is a highly poisonous alkaloid which has been obtained from the Indian plant known as "mohri," at first thought to be the same as the European *Aconitum Napellus*, but now recognised as a distinct species, *Aconitum chasmanthum*. In this paper a full account is given of the properties of the alkaloid and of its principal salts.

Indaconitine ($\text{C}_{37}\text{H}_{47}\text{O}_{10}\text{N}$) is a crystalline alkaloid very closely resembling aconitine from *Aconitum Napellus* in its general properties, but differing, however, in its habit of crystallisation and in many of its physical properties. Most of the salts crystallise well, and are distinct from the corresponding aconitine salts. Its physiological action has been shown to closely resemble that of aconitine and pseudaconitine (Cash and Dunstan, *Proc. Roy. Soc.*, 1905).

Indaconitine undergoes hydrolysis in two stages, in the first of which an acetyl group is eliminated as acetic acid, with the formation of a base, indbenzaconine, which has not been crystallised, but furnishes crystalline salts. This hydrolysis is represented by the equation—



Indbenzaconine is practically non-poisonous. On further hydrolysis, indbenzaconine furnishes benzoic acid and pseudaconitine identical with the final hydrolytic product of pseudaconitine.

Indaconitine is therefore of interest as representing a type of highly toxic alkaloid intermediate in its properties between the aconitine of the common European aconite (*A. Napellus*) and the pseudaconitine derived from the Indian aconite of Nepal. The discovery of this alkaloid and its proximate constitution has led the authors to change the formula of pseudaconitine from $\text{C}_{36}\text{H}_{49}\text{O}_{12}\text{N}$, the formula originally assigned to the alkaloid by Wright, to $\text{C}_{36}\text{H}_{51}\text{O}_{12}\text{N}$.

175. "Contributions to Our Knowledge of the Aconite Alkaloids. Part XVII. Bihhaconitine, the Alkaloid of *Aconitum spicatum*." By WYNDHAM ROWLAND DUNSTAN and ALBERT EDWARD ANDREWS.

This alkaloid, like indaconitine described in the previous communication, is highly poisonous. It has been isolated from a supposed variety of *Aconitum ferox* of India, which has now been proved to be a distinct species, *Aconitum spicatum*. The vernacular name of the plant being "bikh," the name bihhaconitine is proposed for the new base.

Bihhaconitine ($\text{C}_{36}\text{H}_{51}\text{O}_{11}\text{N}$) does not crystallise so readily as other "aconitines," and its physical properties are distinct. A number of its salts have been prepared, and most of them crystallise well. Its physiological action very nearly resembles that of the other aconitines: its toxicity towards warm-blooded animals is greater than that of either aconitine or japaconitine, but is slightly inferior to that of pseudaconitine, which is the most poisonous alkaloid of the group.

Bikhaconitine, like the other aconitines, undergoes hydrolysis in two stages. In the first of these, an acetyl group is eliminated as acetic acid, forming a new base (veratroylbikhaconine). This alkaloid does not crystallise, but furnishes crystalline salts. On further hydrolysis veratroylbikhaconine furnishes veratric acid and bikhaconine, which does not crystallise, but furnishes crystalline salts. This alkaloid differs from other "aconines" previously described.

The paper contains a full account of the properties of bikhaconitine, its salts and derivatives, and a comparison of their properties with those of the other aconitines which have been previously described. The formula of bikhaconitine differs from that of pseudaconitine by one atom of oxygen.

176. "Contributions to Our Knowledge of the Aconit Alkaloids. XVIII. The Aconitine Group of Alkaloids." By WYNDHAM ROWLAND DUNSTAN and THOMAS ANDERSON HENRY.

This paper gave a general account of the properties of the several closely allied "aconitines" which have been described in the course of the present investigation, and also of the non-poisonous alkaloids obtained from varieties of aconitine. It is pointed out that now that it has been established that closely related Indian aconites furnish similar, but nevertheless quite distinct, toxic alkaloids, it is most desirable that a similar examination should be made of the European aconites of the type of *Aconitum Napellus*. The work of Wright, Jurgens, and other chemists, as well as that of the present investigators, renders it highly probable that an examination of European plants commonly classed as *Aconitum Napellus* will reveal the presence of alkaloids very closely resembling, but yet distinct from, aconitine. The evidence already recorded goes to show that the aconitine isolated by Wright from English plants and analysed by him and others, which was described in the course of the present investigation, is a distinct substance from the aconitine of German origin which is now an article of commerce.

PHYSICAL SOCIETY.

Ordinary Meeting, November 10th, 1905.

Dr. C. CHREE, F.R.S., Vice-President, in the Chair.

A PAPER ON "The Question of Temperature and Efficiency of Thermal Radiation" was read by Mr. JAMES SWINBURNE.

It has long been known that various surfaces have different emissivities, and it is generally held that at a given temperature some bodies radiate a larger percentage of their total radiation in the form of light. This view is largely based on some experiments by Evans and Bottomley. Evans's experiments really show that if two filaments A and B of the same area but of low and high emissivities respectively are run to give the same light, the filament A of lower emissivity will give a higher efficiency, and it will give a still higher efficiency if run so as to use the same power as B. This is a natural consequence of the different emissivities, and does not at all show that A gives a higher efficiency at the same temperature as B. Prof. Bottomley's experiments are criticised on the ground that he used no photometer, and his reasoning attacked on the ground that he makes the same slip as Evans in confusing difference of emissivity with difference of efficiency at the same temperature. It is urged that a body A at the same temperature as B cannot give out radiation corresponding to a higher temperature of B; for if it could, and A and B were enclosed in a perfectly reflecting space, A would heat B to a higher temperature than A. It may be said that A can have a higher efficiency than B, not by giving out rays corresponding to B at a higher temperature, but by omitting to give some of the longer radiations that B gives. If this

were true, a hot body might be surrounded by a thin case of A lined inside with a substance which only emitted and absorbed long waves. The case would then take in long and give out short waves, though colder than the source. High efficiency or selective emissivity are always sought in polished grey, or white surfaces like flashed filaments, platinum and other metal wires and rare earths. If there were such a thing, it should be found not in white but in black bodies, as a body which is a specially good radiator of light when hot should be black when cold. Lummer's curves of the distribution of energy for a "black body" and polished platinum are compared, and show somewhat higher efficiency for platinum; but the comparison is difficult. The behaviour of flashed lamps and incandescent gas-mantles is explained by the difference of emissivity, without any need for selective emissivities.

The Secretary read a letter from Dr. J. T. BOTTOMLEY, in which he stated that the author's paper seemed to be to a large extent an attack on his work on radiation. He could not see that Mr. Swinburne had made a single experiment in support of his proposition that "in the case of pure temperature-radiation, the light efficiency is a function of the surface-temperature only." No amount of discussion such as the author asked for could do anything to prove or disprove this proposition. He failed to see that the author had worked out any logical proof of the proposition. The author had assumed that he (Dr. Bottomley) was incapable of matching the light-giving properties of two platinum strips placed side by side and properly arranged for this sort of comparison. The matching is exactly the same in principle as in shadow photometry, and in all the cases cited in the paper to which Mr. Swinburne takes exception, Dr. Bottomley's determinations agreed with those of his assistant, Mr. Evans.

Dr. J. A. HARKER expressed his interest in the paper, and said that the question of radiation was of practical importance in the measurement of high temperatures by electrical resistance methods. He asked if two platinum thermometers, one bright and the other blackened, but identical in other respects, were transferred from an ice-bath into a sulphur-bath, would the final temperatures of the two thermometers be the same, and also would the thermometers approach their final temperatures at the same rate?

Prof. H. L. CALLENDAR, referring to Dr. Harker's questions, stated that if the sulphur-bath was in an isothermal enclosure, the two wires would reach the same ultimate temperature although the blackened one would reach it quicker. The difference, however, would be small. With fine wires the loss of heat by conduction through the gas is more important than the radiation loss. The loss by radiation is proportional to the surface, but the loss by conduction is not, and it therefore becomes relatively more and more important with the fineness of the wire. With regard to the action of incandescent mantles, he thought the author's theory was reasonable and satisfactory.

Mr. MAURICE SOLOMON said he did not agree with Mr. Swinburne's contention that in the case of solids there was no such thing as selective emissivity, but that all bodies at the same temperature radiated light of the same efficiency. Selective emissivity existed in the case of incandescent vapours, and if it was consistent with the laws of thermodynamics in such a case, it could not be inconsistent in the case of an incandescent solid. With reference to the incandescent mantle, the explanation put forward by the author did not seem satisfactory. It was difficult to believe that the very small differences in colour between a thoria, a thoria-ceria, and a ceria mantle could account for the enormous differences in their candle powers.

Prof. W. E. AYRTON referred to experiments which he had carried out which tended to show that the temperature of a Bunsen flame was lowered by an incandescent mantle. He had also found that small pieces of mantle heated in a platinum boat to various temperatures just below the melting-point of platinum never looked brighter than the

platinum. If, however, a small hole was made in the bottom of the boat and coal-gas passed in, the mantle immediately became brilliant.

Mr. SWINBURNE, replying to Dr. Bottomley, said that his main argument was that he had not made experiments. In the investigation of a question such as that considered in the paper, it was possible to prove much by means of experiment, but it was also possible to attack the problem by thermodynamic reasoning. He expressed his interest in the fact that Prof. Callendar had referred to his views as reasonable.

Mr. T. H. BLAKESLEY read a "Note on Constant-deviation Prisms."

It appears that any prism of three faces can be made to give a spectrum in which the light, that occupies the centre of the field of view of the telescope at any moment, has undergone passage through the two refracting surfaces of the prism in such a way that its original angle of incidence is equal to its final angle of emergence. This condition, which in the ordinary employment of the prism is associated with minimum deviation, must be described as isogonal passage, the property which has the minimum value being not the deviation, but the rate of passage across the field of view for a given motion of the prism, to which alone in these instruments motion has to be given to bring different parts of the spectrum into the field, the telescope and collimator both remaining fixed. If any triangle having the angles α , β , γ is adopted as the shape of a prism, the telescope must be set to make one of these angles, say γ , with the line of the collimator. Then the prism being placed in the region between them, a position can be found so that any ray selected will be refracted through one of the sides containing the angle γ , reflected at the side opposite γ , and finally refracted through the remaining side containing γ . On emergence it will be parallel to the telescope, and its passage through the refracting faces will be isogonal. The prism will affect the light to the same degree as one used in the ordinary way, of refracting angle $\beta - \alpha$, would do. The sine of the angle of original incidence is equal to $\mu \cdot \sin(\beta - \alpha)/2$ for every ray occupying the centre of the field of view.

If the prism is turned over but the same angle γ employed, the telescope will remain unaltered but the spectrum will run in an opposite direction to the first. If n similar prisms are piled one upon another, the diameter of the telescope and collimator being large enough to embrace them all, n different parts of the spectrum may be brought into coincidence at the centre of the field of view. Thus such prisms afford an excellent mode of mixing colours. Mr. Blakesley showed the case of two prisms in which the spectra ran in different directions. The top prism was slightly tilted by the insertion of a small piece of silver paper between the prisms. By this means one of the spectra was shifted upwards by a small amount, and one could see in the telescope a band, at top and bottom, of the component colours, and in the centre a band of the resulting colours. It was suggested that spectroscopes on this plan could be advantageously employed in measuring the motion in the line of sight of heavenly bodies, as a line brought into coincidence with itself for a terrestrial source in the two spectra would, in the case of such motion, split up into two moving different ways in the field of view. It was also explained how such prisms could be placed in trains for increased dispersion.

ROYAL SOCIETY OF NEW SOUTH WALES.
General Monthly Meeting, September 6th, 1905.

H. A. LENEHAN, F.R.A.S., President, in the Chair.

The following paper was read :—

"Reinforced Concrete" (Paper III.). By Professor W. H. WARREN, Wh.Sc., M.Inst.C.E., M.Am.Soc.C.E., Challis Professor of Engineering, University of Sydney.

The following matters were dealt with :—

- The adhesion of cement mortar and concrete to steel.
- The experimental determination of the neutral axis in a plain concrete, and also in a reinforced concrete beam, and the curves of strain for loads increasing from zero to the load producing fracture; the determination of the true form of the stress curve from the actual strain curve in a plain and in a reinforced concrete beam.
- The safe working stresses and the fundamental equations recommended for the design of reinforced concrete structure.
- The adhesion of cement mortar and concrete to the steel reinforcement was determined by pulling out specially prepared bars of Bessemer steel from prisms 12 inches long $\times$ 4 inches $\times$ 4 inches cross section, by means of a testing machine.

Pounds per sq. in.

- | | |
|--|-----|
| 1. With steel bars having the natural skin on, after forty-five days' hardening in air .. | 198 |
| 2. With the skin removed and the bars polished, after forty-five days' hardening in air .. | 125 |
| 3. With the skin removed (as in 2), but hardened in water, after forty-five days . | 185 |

The experimental determination (b) was made in a special form of Buckton testing machine, with two hydraulic presses for applying the loads at the ends of the beams tested. Ten beams 72 inches long were tested on supports 40 inches centre to centre, with two overhanging portions each 16 inches long. The apparatus for measuring the lengthening and shortening of the beam between the supports over a length of 40 inches, consisted of eight Marten's mirror extensometers, with a corresponding number of scales and telescopes arranged at different positions in the depth of the beam. The extreme fibre strains were determined by means of four Marten's sector extensometers, and the deflections with dials. The mirror extensometers read accurately to 1/10000 of a millimetre, and it will be observed that the bending moments and corresponding stresses between the supports over a length of 40 inches are constant (neglecting the effect of the weight of the beam itself). Four reinforced beams were exactly alike in composition, age, and reinforcement, and the mean deformations, which differed very slightly from the corresponding individual deformations, were plotted. The strain curves proved that a plane section before flexure is not a plane section after flexure, and that the deviation from the plane is greater as the bending moment increases. Again, the neutral axis moves from the centre of the beam towards the compression side as the bending moment increases. The stress curves determined from the strain curves are fairly straight for a bending moment of about one-third of that producing fracture, but they are curved for greater bending moments approximating closely to parabolas just before fracture. The stress curves determined from the tests of the other reinforced concrete beams confirm these results completely. In the plain concrete beam, without reinforcement, the strain curves were approximately straight lines, and the stress curves deduced from them were curved more on the tension than on the compression side, but in both they approximated closely to parabolic curves; the neutral axis also moved 0.8 of an inch towards the compression side as the bending moment was increased.

In regard to the application of these conclusions to the practical design of reinforced concrete structures, it appears desirable to neglect the tensile stress in the concrete, as it contributes little to the moment of resistance of the beams.

Prof. WARREN read some notes on hardness of different metals, and exhibited a Sclerometer for testing same.

Mr. LENEHAN exhibited and explained a chart showing drift of the s.s. *Pilbarra*, after losing her propeller blades.

CHEMICAL NOTICES FROM FOREIGN
SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

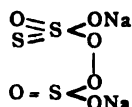
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxviii., No. 13, 1905.

Simple Method of Preparing Pure Monoethyl-aniline from Technical Monoethyl-aniline.—G. Blume and H. Kl. ffer.—If to 97 grms. of the technical product 65 c.c. of concentrated hydrochloric acid are added, a crystalline chlorhydrate separates out after a short time. By leading gaseous hydrochloric acid into the mother-liquors additional small quantities of chlorhydrate are obtained. The total amount is 101 grms., corresponding to a yield of about 80 per cent. The chlorhydrate may then be decomposed by caustic soda, and the oil driven over by steam, dried, and distilled. The distillate is pure monoethyl-aniline.

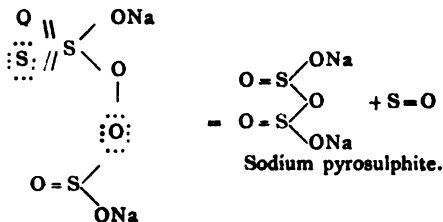
Reduction of Trithionates to Sulphites by Arsenites and Stannites.—A. Gutmann.—When tertiary arsenite acts upon trithionate, sulphite, monosulphoxyarsenate and arsenate are formed, although the formation of the last named was not to be expected, judging from the results of previous researches. Quantitative experiments show that one molecule of trithionate yields one molecule of arsenate, and accordingly gives off one atom of oxygen. The equation appears to be—



The formula of the trithionate is—



which breaks up as follows when treated with a reducing agent:—

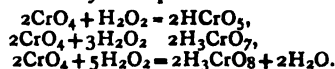


Sodium stannite reduces trithionate in alkaline solution to sulphite, yielding also sulphostannate and stannate. Dithionates do not react with arsenites and stannites, being very stable towards these reagents.

Titanium Trichloride in Volumetric Analysis.—E. Knecht and Eva Hibbert.—The powerful reducing action of titanium trichloride may be employed for the volumetric determination of coloured organic bodies, which form colourless leuco bodies when two atoms of hydrogen are added to the molecule. The coloured substance acts as its own indicator for the titration. To get accurate results the titration must be performed in the absence of air, owing to the fact that the leuco compounds are easily oxidisable. If pure indigotin is sulphonated and the di-sulpho acid is diluted with water and titrated with titanium trichloride in an atmosphere of carbon dioxide after addition of Seignette's salt, a very sharp end reaction occurs, the blue colouration suddenly changing to orange-yellow. The results thus obtained agree very well with the theory. With impure specimens of indigo it is best to remove all impurities from the sulphuric acid solution by neutralising with calcium carbonate. Eosine A, rhodamine B, pararosaniline

chlorhydrate, pararosaniline trisulphonic acid, malachite green, and crystal-violet are among the dye-stuffs which give satisfactory results when titrated thus with titanium trichloride. In the case of the first two, some alcohol must be added, otherwise the solution becomes turbid on titration; probably in consequence of the separation of leuco compound, and the end reaction is not sharp. From these results it appears that titanium trichloride may be used for the quantitative determination of some of the most important basic dye-stuffs (and in some cases of their sulphonated derivatives), and that it gives more accurate results than any other method. If the titanium chloride solution is ready prepared, the determinations (except in the case of indigo) can easily be performed in twenty to thirty minutes. If a dilute solution of the trichloride is added slowly to a solution of hydrogen peroxide a deep orange-yellow colouration is produced, and this reaction may be used for the quantitative determination of hydrogen peroxide. If more trichloride is added the colour of the solution gradually fades, after it has reached a maximum, and disappears altogether as soon as the reduction of the peroxide and the oxidation of the trichloride are complete. For this determination the titanium salt must be free from iron, and the technical product cannot be used. Other inorganic substances to which the authors have applied the same method of determination are ammonium persulphate and metallic tin.

Perchromic Acids.—E. H. Riesensfeld.—If an alkaline aqueous solution of chromic acid is oxidised by means of 30 per cent hydrogen peroxide, red-brown crystals of a salt of the acid H_2CrO_8 are obtained on cooling. If the solution is acidified before the addition of the peroxide blue crystalline salts are obtained, and it is immaterial whether we employ a strong or weak acid (e.g., hydrochloric or acetic acid) or an acid of medium strength (e.g., oxalic acid). These blue salts are much less stable than the red, and are probably identical with the substances which Wiede prepared by adding an alcoholic alkali solution to ethereal perchromic acid solution at a low temperature (-5°). Wiede ascribed to them the formulæ KH_2CrO_7 and $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$. If instead of alkali pyridine is added to a solution of chromic acid anhydride in water, which is then oxidised by means of hydrogen peroxide, a blue crystalline substance of the formula PyHCrO_5 separates out, a derivative of the acid HCrO_5 . Moreover, if the same very dilute solution used to prepare $(\text{NH}_4)_3\text{CrO}_8$ is allowed to stand at the temperature of the room, after twelve to twenty-four hours crystals of the composition $\text{CrO}_4 \cdot 3\text{NH}_3$ separate out, which resemble the crystals of $(\text{NH}_4)_3\text{CrO}_8$ very strongly in appearance, though they are somewhat darker in colour. If a paste is made of $(\text{NH}_4)_3\text{CrO}_8$ and water and acids are added to it, oxygen is given off, and the salt $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$ separates out. When an excess of pyridine is added to a paste either of $(\text{NH}_4)_3\text{CrO}_8$ or $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$, the salt PyHCrO_5 is obtained, and from all three salts, $(\text{NH}_4)_3\text{CrO}_8$, $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$, and PyHCrO_5 , an excess of ammonia gives $\text{CrO}_4 \cdot 3\text{NH}_3$, the most stable of all the higher oxidation products of chromium. All these reactions may be explained by supposing that hydrogen peroxide is either taken up or given up, as represented by the equations:—



All these compounds give a violet-blue colour if their aqueous solutions are treated with ether and acids are added, the tint varying from a reddish violet to a deep indigo blue, according to the amount of oxygen in the chromium compound and the concentration of the acid; the strongly acid solution of the highest oxidation product gives the deepest blue colour. As these substances are formed on the oxidation of aqueous chromic acid solutions, both from the ethereal and aqueous solutions, we may assume that in the blue ethereal so-called "perchromic acid solution" a mixture of these substances is present, and not a single

substance. The empirical formula of these substances may be expressed by $2\text{CrO}_4 + x\text{H}_2\text{O}_2$, the acids of the salts known at present being those for which $x = 1, 3$, and 5 . Compounds derived from an oxide (or acid anhydride) Cr_2O_7 do not produce a blue colouration in the ether, and thus the blue colour is due to the oxide CrO_4 alone and to its derivatives.

Complex Molybdenum Rhodanides.—J. Sand and O. Burger.—If to an acidulated solution of ammonium molybdate and rhodanammionium a reducing agent is added, a dark reddish brown colouration is produced. On addition of ether or amyl alcohol and evaporation of the solvent, a semi-solid mass is obtained. If tertiary bases are added to the ethereal (or amyl) alcoholic extract from the acid solution, well defined crystalline compounds are obtained. For instance, pyridine yields, according to experimental conditions, either brownish red crystals of $\text{Mo}(\text{SCN})_4\text{Py}_2$ (I.) or yellow tablets of $\text{Mo}(\text{SCN})_4\text{Py}_4 + 2\text{PyHSCN}$ (II.). The composition of pyridine compound I. shows that the red rhodanide, easily soluble in organic solvents, is a derivative of tetravalent molybdenum; and the behaviour of pyridine salt II. seems to show that the molybdenum is hexavalent. Four rhodan-residues are precipitated from it by means of silver nitrate. Thus the constitutional formula of salt II. appears to be—



or else $\left[\begin{array}{c} \text{IV.} \\ \text{Mo} (\text{PyHSCN})_2 \end{array} \right] (\text{SCN})_4$. The brown pyridine

salt I. must then be given the formula $\left[\begin{array}{c} \text{Mo Py}_2 \\ (\text{SCN})_4 \end{array} \right]$.

The oxidation products of these substances cannot be determined by titration with permanganate, because of the SCN residue they contain. The brown molybdenum dipyridine tetrarhodamide I. was therefore converted into yellow prisms of $\text{MoCl}_4 \cdot 6\text{PyHCl}$ by the action of hydrochloric acid in acetone solution. This chloride is soluble in water, and all the chlorine in a solution of it in nitric acid can be precipitated as silver chloride.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "Measurement of High Frequency Currents and Electric Waves," by Dr. J. A. Fleming, F.R.S.

WEDNESDAY, 29th.—Society of Arts, 8. "The British Association in South Africa," by Sir William H. Preece, K.C.B., F.R.S.

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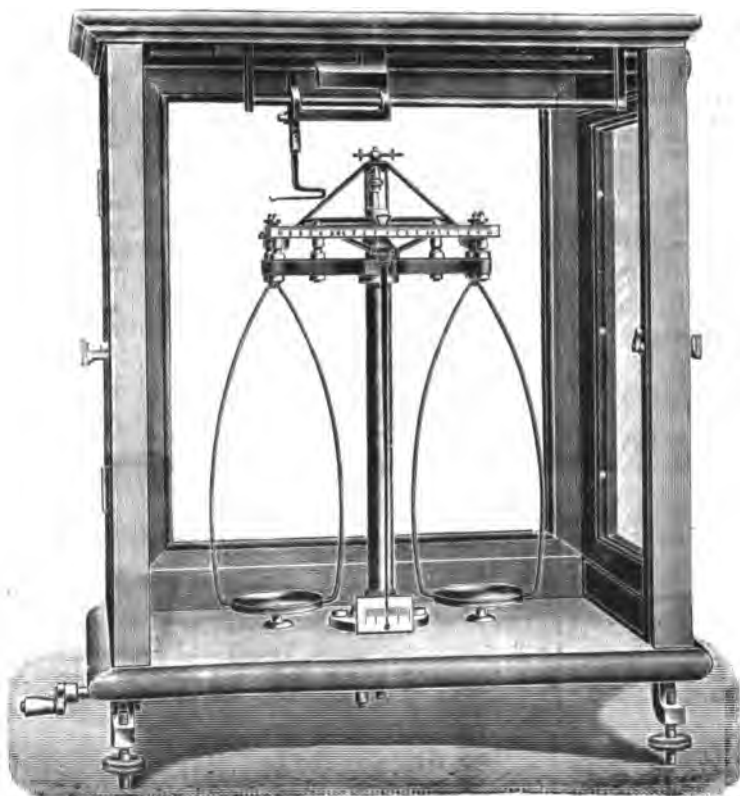
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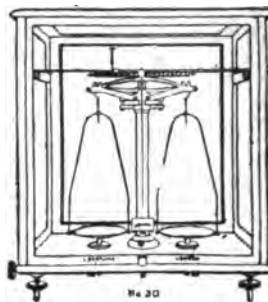
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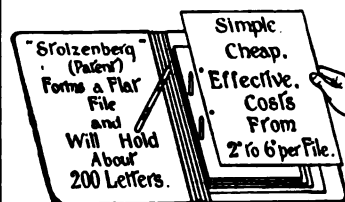
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THE CHEMICAL NEWS.

VOL. XCII., No. 2401.

A NEW RADIO-ACTIVE ELEMENT WHICH EMITS THORIUM EMANATION.

By O. HAHN.

IN March, 1905, a preliminary communication by the author under the above title was brought before the Royal Society of London by Sir William Ramsay (*Proc. Roy. Soc.*, A, lxxvi., 115; *Zeit. Phys. Chem.*, 1905, li., 717). I now propose to give briefly the results of further work on the same subject. These results confirm and supplement the preliminary communication.* The name radio-thorium is proposed for the constant strongly radio-active element, which in all probability forms the active constituent of thorium, which is in itself perfectly inactive. As regards its preparation from the barium-radium mixture, it was first collected in the more soluble liquors of the fractionation, and then precipitated together with some iron by means of ammonia. It thus appeared that this fractionation method, even after it had been applied repeatedly, did not lead to the desired result. Another method of separation was therefore sought; a drop of iron chloride solution was added to each separate radium fraction, which all contained radio-thorium as well, and then the iron was precipitated by means of ammonia. In this case also no quantitative separation from radium was effected; moreover, some radium was always to be found in the ammonia precipitates.

A separation by means of sulphuric acid was not possible either, as the radio-thorium would be carried down also.

By repetition of the methods stated, however, a satisfactory separation of the radio-thorium from the radium could be effected.

Then a greater difficulty lay in the concentration of the radio-thorium precipitates. Chemically these consist principally of iron and an element belonging to the rare earths, whose nature is not yet known. It does not seem to be thorium.

The method first employed to separate the radio-thorium from the greater part of the iron by means of ammonium oxalate or oxalic acid is not suitable, because the further working up of the oxalates—which naturally amount only to some m.grms.—is difficult to perform without loss. Single precipitations are not generally successful, and a fractionation mechanism must always occur. The "carbonate separation" gives fairly good results. The acid solutions were precipitated with ammonium carbonate in excess in the cold. On boiling the filtrate some basic carbonate separated out; this was relatively more strongly active than the carbonate precipitated in the cold. Shortly after the precipitation the activity relations are indeed somewhat altered, as thorium X is concentrated more in the first precipitate, and in the second precipitate it has to be formed anew. In this case also many repetitions are prevented, owing to the fact that the quantities rapidly become too small. Up to the present, by far the strongest product obtained was 10.9 m.grms. of a dirty brownish substance which was by no means elementary. It gives off almost 700,000 times as much emanation as an equal weight of ordinary thorium under the same conditions; the 10.9 m.grms. thus correspond in activity to about 7½ k.grms. of thorium of ordinary activity. Besides this quantity, smaller quantities of less activity are present; but it is hardly possible with the material obtainable to get a greater concentration or to obtain more.

As regards the properties of radio-thorium, the name expresses that it possesses the radio-active properties of thorium. It was already apparent from the constancy of the activity that something besides thorium X is present. A preparation kept for more than half a year showed no trace of decrease of activity. The activity of thorium X would have fallen to half its value in four days. The first decomposition product of radio-thorium is precisely this thorium X. The latter may be separated from the constantly active part in the usual way by precipitation with ammonia. The time in which the thorium X sinks to half its value was found to be 4.1 days. The decay constant λ is 106×10^{-6} . The correct number may differ from this within narrow limits; for reasons given at the place cited, the measurements which have been taken are not entirely free from objection. Rutherford and Soddy give the time as four days.

The emanation was investigated most thoroughly. As the mean of a great number of emanation measurements agreeing very well among themselves, with the most varied radio-thorium preparations the value 1.3×10^{-4} was found for λ ; thus the emanation sinks to half its value in 53.3 seconds. For thorium emanation other investigators have found 51.2 and 54 seconds. The extraordinarily large quantity of emanation naturally produces very characteristic phenomena in the dark room; these phenomena are externally hardly distinguishable from those exhibited by actinium emanation. If the little glass vessels containing the 10.9 m.grms. of the substance on a filter wrapped in paper are opened, the emanation spreads itself in clouds over the zinc sulphide screen, and naturally on blowing the characteristic luminescence disappears. It is noteworthy that the emanation rises, and does not sink, as was supposed. If we do not wish to abandon the usual idea that all radio-active elements are those with high atomic weights, no explanation of this can be given; a measurably higher temperature than the surroundings could not be established. The actinium emanation, moreover, shows this property very clearly, while the radium emanation, which is visible even without a screen, undoubtedly behaves like a heavy gas.

As the thorium emanation always needs two to three minutes to collect, after blowing away the emanation the vessel must be closed again for two or three minutes in order to reach the maximum of luminous effect.

According to Rutherford's researches, solid thorium compounds behave very differently as regards their power of emanation; specimens "de-emanated" by ignition give off only very little emanation, and in this respect closely resemble radium, which in the solid state yields only very small quantities of radium emanation. The agreement of radio-thorium with "ordinary" thorium is shown here also. The moving emanation is no longer to be seen after strongly igniting my radio-thorium preparations, but the direct luminescence action on the zinc sulphide and platinum screens is considerably increased. All the induced activity is stored up in the preparation; the total activity is thus greater after ignition than before. As the thorium emanation is condensed by liquid air, by immersion in liquid air we obtain for a moment the same result as by ignition. The emanation condenses in the preparation, the induced activity accumulates till equilibrium is reached, and the preparation becomes more strongly active. After being taken out it again becomes more feeble in the same proportion. Radio-thorium itself is not luminescent, but the glass vessels in which a very strong preparation is kept show to an experienced eye distinct fluorescence in the dark. Just as with actinium or Giesel's emanium, the strong radio-thorium preparations make objects which are brought close to them strongly radio-active. If some paper is introduced into the glass vessel which contains the 10.9 m.grms. of the strongest substance, the paper after some hours shows very powerful luminescent action on the screen. This induced activity on the paper naturally cannot be indefinitely increased; if radio-active equilibrium is produced it remains constant as

* A more complete description of the preparation and properties of the active substance appeared in the October number of the *Jahrbuch für Radioaktivität und Elektronik*. The discussion of the name radio-thorium will also be found there.

long as it is in the neighbourhood of the preparation. If it is removed the induced activity naturally diminishes. The so-called scintillation of the α -rays may be seen vividly with objects thus made active by induction.

To measure the decrease of the induced activity three different methods of preparation were used. The first method was that frequently employed formerly, viz., concentration on the negatively electrified rod or wire.

A second method of preparation often used in this work was the condensation of the emanation by means of liquid air in a glass spiral, solution of the induced activity in dilute acid, and evaporation on a clock glass or in a small dish.

The simplest method is that already touched upon above:—An object is brought into the neighbourhood of the strong preparation; after a day it is removed, and the decrease is measured in the electroscope or electrometer. One of the latter is naturally always necessary for the quantitative measurements. As the mean of several series of measurements the decay constant $\lambda = 1.82 \times 10^{-4}$ was found. The time in which the half value is reached amounts to 10.6 hours; formerly eleven hours was mostly assumed for this value, but more recently 10.6 seems to have been found by another investigator also. The splitting up of induced thorium activity into thorium A and thorium B recently performed by two workers is naturally not affected by it (J. M. W. Slater, "Inducirte Activität des Thoriums," *Chem. Centralbl.*, 1905, i., 1629; W. von Lerch, *Ibid.*; *Ber. d. Wiener Akad.*, March 2, 1905).

As yet not much is known concerning the chemical properties of radio-thorium. The smallness of the quantities available render its investigation very difficult, perfectly quantitative precipitations of the activity are never effected, and many chemical operations may therefore easily produce a very considerable "dilution" of the substance. The reactions of radio-thorium appear to be those of the rare earths, as was to be expected. But whether radio-thorium behaves chemically exactly like radium is very doubtful, and some phenomena argue against it.

In all chemical experiments we must take into account thorium X, which under some circumstances causes deviations. Therefore the measurements must always be performed at least twice at different times. The fact that radio-thorium is often carried down by all precipitates in fairly considerable quantity may easily lead to errors as regards chemical relationships.

The reasons that argue in favour of radio-thorium being the radio-active constituent of thorium, which is itself inactive, are more fully discussed elsewhere (*cf.* also Backur, *Ber.*, 1905, xxxviii., 1756); they led also to the choice of name. The occurrence and behaviour of radio-thorium seem to show the possibility of its being the first slow decomposition product of thorium. Between thorium and radio-thorium there would thus exist a genetic connection similar to that which exists between uranium and radium, and which has recently been proved experimentally by Soddy's investigations (*Phil. Mag.*, [6], ix., 768; *cf.* Boltwood, *Am. Journ. Sci.*, [4], xx., 239).—*Berichte*, 1905, xxxviii., 3371.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

(Continued from p. 243).

Behaviour of Solutions of the Double Fluorides of Columbium and of Titanium with a variety of Bases.

Excess of sodium hydroxide was found to precipitate titanium completely from a solution of potassium-titanium fluoride, while with potassium-columbium oxyfluoride it gave a precipitate soluble in slight excess, but again insoluble and separating in a crystalline form from a large

excess of the sodium hydroxide. The precipitate formed in the case of the titanium was insoluble in water, while, in the case of columbium, the crystalline deposit was completely soluble in hot water. It was hoped that this difference of behaviour might afford a means of separating these two elements. To test this, experiments were tried as follows:—

1. 0.9600 grm. of $K_2CbOF_5 \cdot H_2O$, containing 0.4272 grm. of Cb_2O_5 , and 1.1600 grm. K_2TiF_6 , containing 0.3753 grm. of TiO_2 , were dissolved in 200 c.c. water, brought to boiling, and an excess of sodium hydroxide added. The precipitate which formed was partly crystalline and partly flocculent. The solution was allowed to stand over night. The precipitate was filtered out, drained, and washed back into a platinum dish. It was covered with 200 c.c. of water, brought to boiling, filtered hot, and washed with hot water. The filtrate, which should contain most of the columbium and none of the titanium, was brought to boiling, and sulphuric acid and ammonium hydroxide added. The hydrate obtained was ignited to oxide and weighed 0.1640 grm. It was found to contain 0.0117 grm. of TiO_2 . The titanium content was determined colorimetrically by fusing with potassium acid sulphate, dissolving the fusion in oxalic acid, and comparing the colour developed with hydrogen peroxide with that of a titanium solution of known strength in oxalic acid.

Part insoluble—0.2749 Cb_2O_5 , 0.3636 TiO_2 .

$TiO_2 \cdot 4Cb_2O_5$, soluble portion; $Cb_2O_5 \cdot 4TiO_2$, insoluble portion.

2. A mixture containing 0.1270 grm. K_2TiF_6 , or 0.0423 grm. TiO_2 and 2.5280 grms. $K_2CbOF_5 \cdot H_2O$, or 1.1376 grms. Cb_2O_5 , was treated as above. The precipitate was nearly all crystalline. That part of it insoluble in water weighed 0.0470 grm. and contained 0.0074 grm. TiO_2 , leaving 0.0349 grm. of TiO_2 in solution (by far the greater quantity).

3. 0.2830 grm. K_2TiF_6 , containing 0.0943 grm. TiO_2 , and 2.7040 grms. $K_2CbOF_5 \cdot H_2O$, containing 1.2168 grms. Cb_2O_5 , were treated as before. The precipitate was chiefly crystalline. A small part of it was flocculent. The part insoluble in water weighed 0.0740 grm. and contained 0.0148 grm. TiO_2 , showing that 0.0795 grm. TiO_2 went into solution and would be found with the bulk of the columbium.

4. 0.6790 grm. K_2TiF_6 , containing 0.2263 grm. TiO_2 , and 2.2530 grms. $K_2CbOF_5 \cdot H_2O$, containing 1.0139 grms. Cb_2O_5 , were treated as before. The precipitate contained a considerable amount of flocculent material. The part insoluble in water weighed 0.1720 grm. and contained 0.0710 grm. TiO_2 , leaving 0.1553 grm. of TiO_2 in solution.

The action of potassium hydroxide was also tried. It gave a precipitate with columbium, soluble in an excess and re-precipitated by greater excess. When the solution was evaporated, pearly plates of potassium columbate separated out. With a solution of K_2TiF_6 a heavy precipitate was obtained, but the filtrate gave a slight test for titanium.

1.3130 grms. K_2TiF_6 , containing 0.4377 grm. of TiO_2 , and 1.0060 grm. $K_2CbOF_5 \cdot H_2O$, containing 0.4467 grm. Cb_2O_5 , were dissolved in 200 c.c. of water and the solution brought to boiling, when an excess of potassium hydroxide was added. The precipitate obtained weighed 0.5900 grm. after ignition. The filtrate gave a very pronounced test for titanium.

Solutions of K_2TiF_6 and K_2CbOF_5 were studied with various organic bases in the hope that differences of behaviour might present themselves which would lead to a quantitative separation of these two elements. (See Table).

The behaviour of the bases which react with the above solutions of titanium and columbium may be divided into the following classes:—

1. Those which precipitate the titanium completely, and while they precipitate the columbium dissolve it upon the addition of an excess of the reagent to form columbates.

* *Proceedings of the American Philosophical Society*, 1905, xlv., p. 177.

Reagent.	Solution of K_2TiF_6 .	Solution of K_2CbOF_6 .
1. Monomethylamine	Precipitation complete.	Precipitate soluble excess.
2. Dimethylamine	" "	" "
3. Trimethylamine	" "	" "
4. Tetramethylamine	" "	" "
5. Monoethylamine	" "	" "
6. Diethylamine	" "	" "
7. Triethylamine	" "	Precipitate by large excess; insoluble excess; difficultly soluble in water. Precipitate soluble excess.
8. Dipropylamine	" "	" "
9. Amylamine	" "	" "
10. Isobutylamine	" "	" "
11. Allylamine	" "	" "
12. Ethylenediamine	" "	" "
13. Propylenediamine	" "	" "
14. Butylenediamine (secondary)	" "	" "
15. Butylenediamine (normal)	" "	" "
16. Hexylamine	" "	" "
17. Benzylamine	" "	" "
18. Benzylmethylamine	" "	" "
19. Piperidine	" "	" "
20. Camphylamine	" "	Precipitate slightly soluble excess.
21. Dibenzylamine	" "	Precipitation complete.
22. Pyridine	" "	" "
23. Di-isobutylamine	" "	" "
24. Tripropylamine	" "	" "
25. Diamylamine	" "	" "
26. Heptylamine	" "	" "
27. Toluylenediamine (meta)	Partial precipitation.	" "
28. Picoline	" "	" "
29. Tri-isobutylamine	Slight precipitation.	Precipit. nearly but not quite complete.
30. Bornylamine	" "	Precipitation not complete.
31. Aniline	Precipitation not complete.	Precipitation heavy, but not complete.
32. Toluidine (m)	Slight precipitation.	" "
33. Monomethylaniline	Slight precipitation after 24 hours.	" "
34. Mono-ethylaniline	Slight precipitation on standing.	Precipitation slow; incomplete.
35. Isoquinoline	" "	Precipitation heavy; incomplete.
36. Quinoline	" "	Precipitation nearly complete.
37. Hexamethylenetetramine	" "	Precipitation heavy; incomplete.
38. Bromaniline (m)	No precipitation.	Slight precipitation on standing.
39. Chloraniline (o)	" "	" "
40. Dichloraniline	" "	" "
41. Diethylaniline	" "	" "
42. Chloraniline (p)	" "	" "
43. Dimethylaniline	" "	" "
44. Xylidine (p)	" "	Precipitation slow; incomplete.
45. Xylidine (o)	" "	" "
46. Xylidine (m)	" "	" "
47. Tetrahydroquinoline	" "	Slight precipitation on standing.
48. Benzylaniline	" "	No precipitation.
49. Diphenylamine	" "	" "
50. Tribenzylamine	" "	" "
51. Naphthylamine (p)	" "	" "
52. Naphthylamine (o)	" "	" "
53. Nitronaphthalene	" "	" "
54. Bromphenylhydrazine	" "	" "
55. Nitrophenylhydrazine	" "	" "
56. Benzidine	" "	" "
57. Nitraniline (o)	" "	" "
58. Nitraniline (p)	" "	" "
59. Nitraniline (m)	" "	" "
60. Diphenyl	" "	" "
61. Diphenyl carbonate	" "	" "
62. Methyl carbonate	" "	" "
63. Ethyl carbonate	" "	" "
64. Piperine	" "	" "
65. Monochlorhydrin	" "	" "
66. Trichlorhydrin	" "	" "
67. Dibromhydrin (p)	" "	" "
68. Nitrosodipropylene	" "	" "
69. Nitrosodiethylene	" "	" "
70. Nitrosodimethylene	" "	" "
71. Succinimide	" "	" "
72. Methyl diphenylamine	" "	" "
73. Tetranitromethylaniline	" "	" "
74. Bromaniline	" "	" "

This class, while showing pronounced difference of behaviour, is useless as a means of separation, for upon treating a solution containing both titanium and columbium with one of these reagents the titanium was found both in the soluble and in the insoluble portion. Columbium was also found in the titanium precipitate. The probable explanation for this is that a columbate was formed which dissolved the freshly precipitated titanium hydrate to a salt of a complex titanocolumbic acid, which was soluble, and also a small amount of an acid salt or a free acid containing an excess of titanium, which was insoluble.

2. To the second class of reagents belong those which precipitate the hydrates of the two elements, and are not sufficiently basic to dissolve the columbium hydrate and form columbates. Those reagents which are sufficiently basic to completely precipitate the columbium are strong enough to partially precipitate the titanium. Quinoline seemed the most promising of all the reagents which were tried.

3. Those reagents which gave only a partial precipitation with columbium and no precipitation with titanium solutions did not precipitate columbium hydrate free from titanium, from a solution containing both titanium and columbium. The hydrate precipitated always gave a strong test for titanium after dissolving it in oxalic acid. This may have been due in part to the extreme difficulty encountered in washing the precipitate free from mother-liquor.

4. The remaining reagents precipitated neither titanium nor columbium.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FROM THE 1ST TO THE 21ST OF OCTOBER, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, November 9th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 144 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 21st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 144 samples examined by us during the month, all were clear, bright, and well filtered.

Again we have to record a deficit of rain at Oxford. The rainfall registered during October is 1.40 inches. The average rainfall is 2.76 inches; thus we have the rather large deficit of 1.36 inches, which, if added to the previous one of 2.34 inches, makes a total deficit of 3.70 inches for the first ten months of this year, or 17.7 per cent on the thirty-five years' average.

TABLE A.—Rainfall in Inches at Oxford, Month by Month, during the Year 1905.

	Actual fall.	Mean of 35 years.	Difference from the mean.	
	Inches.	Inches.	Inches.	Inches.
January ..	0.78	2.08	-1.30	—
February ..	0.39	1.80	-1.41	—
March ..	2.96	1.47	—	+1.49
April ..	1.94	1.61	—	+0.33
May ..	0.79	1.75	-0.96	—
June ..	4.15	2.10	—	+2.05
July ..	0.16	2.49	-2.33	—
August ..	3.27	2.38	—	+0.89
September ..	1.29	2.39	-1.10	—
October ..	1.40	2.76	-1.36	—
	17.13	20.83	-8.46	+4.76

Our bacteriological examinations of 262 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 453 others from special wells, standpipes, &c., making a total of 715 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 17 samples) ..	66
New River, filtered (mean of 51 samples) ..	3
Thames, unfiltered (mean of 18 samples) ..	35.177
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 140 samples) ..	16
Ditto ditto ..	highest 310
Ditto ditto ..	lowest 0
River Lea, unfiltered (mean of 18 samples) ..	87
River Lea, from the East London District clear-water wells (mean of 18 samples) ..	16

Of the 209 daily samples taken from the general filter wells of the Metropolitan Water Board, twenty-four samples, or 11.4 per cent, were sterile. Five samples, or 2.3 per cent, contained more than 100 microbes, and of these three samples contained more than 150 microbes per c.c. The five excess samples contained an average of 225 microbes per c.c. In September the one excess sample contained 110 microbes per c.c.

One very exceptional circumstance we have to record during the past month, and that is the extraordinary microbic condition of the River Thames. Between the 12th and the 18th the microbes rose from 320 to over a quarter of a million per c.c., and then as rapidly declined.

During the past ten months we have examined 10,712 samples of water bacteriologically, as compared with 9146, 8822, 6953, and 6893, respectively in the four previous years. We have also made 2312 chemical analyses of London waters during this period, making a total of 13,024 samples examined during the first ten months of this year.

Table B gives the bacteriological results for the past ten months. During the first six months the Thames-derived Districts' clear-water wells contained on an average 21 bacteria per c.c., while the New River, Lea, and Kent supplies contained 11, 22, and 9 respectively. During the past four months the numbers of bacteria from the same four sources were 21, 10, 18, and 10 respectively.

Table D gives the average chemical composition of the Thames-derived supplies during the year 1905. It will be observed that the amount of organic matter has been very low during the whole of this period, and exceptionally so during the past three months.

In presenting our final report, we take the opportunity of stating that we commenced the systematic examination of the London water in the autumn of 1880, and so have completed twenty-five years of continuous supervision of the chemistry and bacteriology of the Metropolitan Water Supply. During this period we have made chemical

TABLE B.—Showing the Average Monthly Bacterial Variations during the Year 1905.

Month.	Thames, unfiltered.	Thames- derived supplies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered.	River Lea (East London District), filtered.	Kent District, unfiltered.
January	4300	29	381	15	164	13	13
February	1392	13	220	8	174	27	30
March	8078	6	152	3	105	3	9
April	4887	19	106	13	175	27	3
May	1056	24	147	16	205	23	2
June	4493	38	206	16	264	41	1
	4034	21	202	11	181	22	9 Mean of 1st 6 months.
July	6287	34	306	14	335	21	2
August	2535	21	146	18	330	28	23
September	2341	10	102	6	157	7	5
October	35177	16	66	3	87	16	—
	11584	20	155	10	227	18	10 Mean of next 4 months.
	7809	20	178	10	204	20	9 Mean of 10 months.

TABLE C.—Average Number of Microbes in the Filtered London Waters for the Past Nine Years.

	Thames-derived supplies.	New River.	River Lea.
1897	46	32	62
1898	34	30	25
1899	27	15	20
1900	21	9	10
1901	24	10	22
1902	27	13	25
1903	36	16	26
1904	20	10	14
1905 (10 months)	20	10	20

TABLE D.—Averages of the Supplies derived from the River Thames during the Year 1905.

	Common salt per gallon. Means.	Nitric acid per gallon. Means.	Hardness. Degrees. Means.	Oxygen required per gallon. Means.	Organic carbon per gallon. Means.	Organic carbon per gallon. Maxima.	Colour. Brown : Blue. Means
January	2'319	1'069	16'14	0'035	0'109	0'167	15'9 : 20
February	2'268	1'076	16'06	0'027	0'095	0'128	13'5 : 20
March	2'255	0'951	15'02	0'032	0'112	0'186	13'1 : 20
April	2'232	0'818	15'16	0'041	0'142	0'206	16'1 : 20
May	2'101	0'853	13'97	0'032	0'097	0'115	14'0 : 20
June	2'079	0'725	13'18	0'044	0'132	0'201	15'7 : 20
July	2'111	0'656	13'10	0'046	0'117	0'161	18'3 : 20
August	2'235	0'599	12'95	0'036	0'097	0'125	16'1 : 20
September	2'181	0'547	12'92	0'030	0'081	0'104	13'7 : 20
October	2'278	0'719	13'07	0'028	0'087	0'102	12'5 : 20

analyses of 58,489 samples and bacteriological examinations of 61,081 samples, making a total of 119,570 samples.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, November 2nd, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. W. B. Tuck, J. W. White, and E. W. Bealey were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Adam Lawson Kelly Adam, 296, Bath Street, Glasgow; C. Chester Ahlum, Lansdale, Pennsylvania, U.S.A.; James Edward Alcock, 42, Gill Street, Moston

Lane, Blackley; James Albert Allison, Luchana Laboratory, Apartado, 45, Bilbao, Spain; George Henry Barbrook, Stowmarket, Suffolk; Marmaduke Barrowcliff, 25, Priory Road, Kew, Surrey; John Coggin Brown, B.Sc., Fairleigh, Cockton Hill, Bishop Auckland; Joseph Edward Coates, B.Sc., Sunny Side, Oakamoor, Stoke-on-Trent; Douglas Henry Bellars Cowman, Heathville Corner, Gloucester; Arthur Augustine Dallman, Lyndhurst, Prospect Vale, Liverpool; John Llewelyn Davies, B.A., 8, Rugby Road, Neath; John Doull, 8, Lauriston Place, Edinburgh; John Beaconsfield Gall, Knoxland, Erith Road, Belvedere, Kent; Sidney Montague Haig, St. Edmund's Avenue, Port Hill, Stoke-on-Trent; Alfred Hart, M.A., B.Sc., Norman Avenue, Hawksburn, Victoria, N.S.W.; Jack Vernon Johnson Hayman, Tringhurst, Cranleigh, Surrey; John Michael Higgins, 39, Queen Street, Melbourne, Australia; William Basil Hill, Eastfield, Stockton Lane, York; Isaac Berkwood Hobsbaum, 79, Claremont Road, Forest Gate, E; Cecil Hollins, 34, Beamsley Road, Frizinghall, Yorks.; Maurice Brooks Jack, 66, Burma Road, Clissold Park, N.; Edward Towyn Jones, B.Sc., 17, Bloomsbury Square, W.C.; Rudolph Lyon, 400, Huddersfield Road, Halifax; William McCleary, 61, Station Road, Pendlebury, Manchester; Robert Drysdale MacKechie, c/o Messrs. A. Boake, Roberts, and Co.,

Ltd., Stratford, E.; Harry Martin, 14, Hardman Street, Liverpool; Harry George Fletcher Micklewright, B.A., 116, St. James's Road, Croydon; Edalji Manekji Modi, opposite Grant Road Station, Bombay; John Motion, Edgewater, New Jersey, U.S.A.; Henry Allen Dugdale Neville, B.Sc., 81, Revidge Road, Blackburn; Francis Richard Penn, Highborne Terrace, Shadwell Lane, Moortown, Leeds; Hugh Donald Perkins, Dodwell, Bursledon, Hants; Percy Barker Phipson, c/o J. Staples and Co., Ltd., Wellington, N.Z.; Frederick John Pooler, B.Sc., The Boys' High School, Grahamstown, Cape Colony, South Africa; James Frederick Fothergill Rowland, B.A., 5, St. James's Park, Croydon; Harold Marmion Royle, 12, Barfield Villas, George Lane, S. Woodford; Harry Nestor-Schnurmann, Corinth House, Cheltenham; Douglas Temple Setterington, 45, Regent Road, Blackpool; John Booty Tillott, 55, Wood Street, Westminster, S.W.; Frank Tutin, 49, The Avenue, Kew, Surrey; George Stanley Walpole, 349, Queen's Road, Battersea Park, S.W.; John Ledger White, D.Sc., 73, Cambridge Mansions, Battersea Park, S.W.; Gerard William Williams, B.A., P.O. Box, 21, Germiston, Transvaal, South Africa.

The PRESIDENT referred to the loss sustained by the Society in the death of Professor P. T. Cleve, who was elected an Honorary and Foreign Member in February, 1883, and who died on June 18th, 1905; also in the death of Mr. G. B. Buckton, F.R.S., who was elected a Fellow in March, 1852.

Of the following papers, those marked * were read:—

*177. "Molecular Conductivity of Water." By PHILIP BLACKMAN.

The molecular conductivity of water may be represented by K and calculated from the equation—

$$\mu\nu_{HX} + \mu\nu_{M_1OH} - \mu\nu_{M_1X} = K.$$

The value of K is dependent on (1) temperature, (2) molecular concentration, and (3) nature of the acid ($\mu\nu_{HX}$, $\mu\nu_{M_1OH}$, $\mu\nu_{M_1X}$ represent respectively the molecular conductivities, measured at the same temperature and molecular concentration, ν , of the acid HX, the base M_1OH , and the salt M_1X).

The conclusion is drawn that the greater the value of K the stronger is the acid, taking into consideration (1) the temperature and (2) the molecular concentration. This furnishes a method for determining the relative strengths of acids.

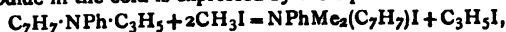
*178. "The Stereoisomerism of Substituted Ammonium Compounds." By HUMPHRY OWEN JONES.

The existence of Wedekind's isomeric α - and β -phenylbenzylmethylallylammonium iodides is so difficult to reconcile with the absence of isomerism in all the other compounds of the same type, that the author has examined these compounds in the hope of obtaining some information about this unique example of isomerism, and has found that the two compounds are not isomerides, but different compounds.

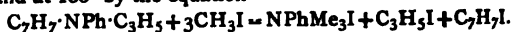
The β -compound dissociates partially into benzyl iodide and tertiary amine in chloroform solution, but is not transformed into the α -compound; it is also completely converted into phenyltrimethylammonium iodide when heated at 100° with methyl iodide in molecular proportions, whereas the α -compound requires twice as much methyl iodide to convert it into phenyltrimethylammonium iodide and benzyl and allyl iodides. Analysis and a comparison of properties prove conclusively that the β -compound is phenylbenzylmethylammonium iodide.

The analyses of the compound previously given by Wedekind and by Hantzsch and Horn are incorrect, and the reactions described by the last-named chemists can only have been obtained with impure material.

The reaction between benzylallylaniline and methyl iodide in the cold is expressed by the equation—



and at 100° by the equation—



At present optical activity is the only evidence of stereoisomerism of quinquivalent nitrogen compounds of the type NabcdX, and, since the search for isomerides has been so thorough, it is concluded that no isomerides can be produced by the union of tertiary amines and alkyl iodides.

The hypothesis suggested by the author (*Trans.*, 1903, lxxxiii., 1403) to account for the non-formation of isomeric quinquivalent nitrogen derivatives from tervalent compounds is now adequate to explain all the known facts, and has been further developed.

DISCUSSION.

Mr. A. W. HARVEY stated that he had prepared considerable quantities of benzylphenylmethylallylammonium iodide, and that when the compound is produced by mixing molecular quantities of carefully purified benzylmethyl-aniline and allyl iodide in an equal volume of mixed methyl and ethyl alcohols (1-9) no trace of Wedekind's β -compound is formed; the reaction goes quite quantitatively, and yields a clean and pure solid product.

Dr. JONES, in reply, said that the β -compound was not produced together with the α -salt when allyl and benzyl iodides were added to the corresponding tertiary amines, but only when methyl iodide was used.

In reply to a question by Dr. Lapworth, the author stated that the evidence for the replacement of allyl by methyl in benzylallylaniline by the action of methyl iodide in the cold was quite conclusive, the benzyl group being only removed on heating.

*179. "Note on the Fluorides of Selenium and Tellurium." By EDMUND BRYDGES RUDHALL PRIDEAUX.

The fluorides of selenium and tellurium are both gaseous substances prepared by the action of fluorine on the elements, their densities corresponding to the formulae SeF_6 and TeF_6 respectively. They are easily condensable by cold alone, forming white snow-like solids, the vapour pressure curves of which will be published shortly along with an account of the other properties of the gases.

DISCUSSION.

Mr. BLISS asked whether the author could give any further information as to the nature of the solid fluorides isolated by Moissan.

Mr. PRIDEAUX, in reply, said that the solid fluoride of tellurium left in the reaction tube may be the tetrafluoride, TeF_4 , described as being obtained by the action of hydrogen fluoride on tellurous acid, but is more probably an oxyfluoride.

*180. "The Constitution of Glutaconic Acid." By JOCELYN FIELD THORPE.

The "double bond" in glutaconic acid,—



is apparently not fixed, since the reactions of this substance clearly indicate that it possesses a symmetrical structure.

Thus $\alpha\beta$ -dimethylglutaconic and $\beta\gamma$ -dimethylglutaconic acids, prepared by methods which leave no doubt as to their constitution, are not isomeric but identical. α -Methyl- β -ethylglutaconic acid and β -methyl- γ -ethylglutaconic acid are also identical.

Derivatives of glutaconic acid are produced when ethyl cyanoacetate or its monoalkyl derivatives react with ethyl acetoacetate or its monoalkyl derivatives, the ethyl salts formed yielding either (1) derivatives of glutaconic acid or (2) derivatives of 2:6-dioxypyridine, according to the nature of the hydrolysing agent and the constitution of the salt.

*181. "Some Alkyl Derivatives of Glutaconic Acid and of 2:6-Dioxypyridine." By HAROLD ROGERSON and JOCELYN FIELD THORPE.

Methods for the preparation of all the methyl derivatives of glutaconic acid are described, as well as the modes of preparation and properties of the corresponding derivatives of 2:6-dioxypyridine.

*182. "Notes on the Formation of β -Methylglutaconic Acid and of $\alpha\beta$ -Dimethylglutaconic Acid." By FRANCIS VERNON DARBISHIRE and JOCELYN FIELD THORPE.

By the elimination of hydrogen bromide from ethyl α -bromo- β -methylglutarate a mixture is obtained from which β -methylglutaconic acid can be isolated, the residue consisting of the lactone ethyl salt and the corresponding acid of the trimethylene ring.

From ethyl α -bromo- $\alpha\beta$ -dimethylglutarate, similar products are formed, only in this case a much larger quantity of the glutaconic acid ($\alpha\beta$ -dimethylglutaconic acid) can be obtained.

*183. "The Influence of Water and Alcohols on the Boiling-point of Esters. I. A Modification of Markownikoff's Method of Preparation." By JOHN WADE.

Ethyl acetate forms binary and ternary mixtures of minimum boiling-point with ethyl alcohol and water. The ternary mixture, which contains 9 per cent of alcohol and 8 per cent of water, boils constantly at 70.3° , whilst the binary mixtures, which contain respectively 8.6 per cent of water and 30.6 per cent of alcohol, boil constantly at 70.5° and 71.8° . Most esters form such mixtures with their constituent alcohols and water, and in preparing esters from acids and alcohols by Markownikoff's method of continuous distillation in presence of sulphuric acid (*Ber.*, 1873, vi., 1177), ternary mixtures are therefore usually obtained.

As the Markownikoff interaction, unlike the etherification process on which it is based, now proves on investigation to proceed in most cases readily at 100° , and in presence of any strong acid, it may be modified to afford a general and practical automatic method of preparing these ternary mixtures and their constituent esters in quantity. The lower alkyl esters of formic, acetic, propionic, and butyric acids have been made in this way under ordinary pressure, and various less volatile esters at the same temperature under somewhat reduced pressure. Owing to the peculiar relation of the binary to the ternary mixtures the excess of alcohol may often be removed from these products by distillation with water and fractionation.

*184. "Note on Bromine Fluoride." By EDMUND BRYDGES RUDHALL PRIDEAUX.

Fluorine when passed over bromine combines with it, as stated by Moissan, who has described the appearance of the reaction ("Le Fluor et Ses Composés"). The product, which is more unstable than iodine fluoride and decomposes water with great violence, has not been described. It is a pale yellow liquid with a specific gravity less than that of bromine, and freezes to a white solid which melts at -2° . The analysis of this fluoride leads to the formula BrF_3 , and this compound appears to be the only definite fluoride of bromine.

185. "Solution and Pseudo-solution." (Part IV.). By ERNEST LINDER and HAROLD PICTON.

The authors have completed, so far as they are able, the study of solution and pseudo-solution originated by them in 1892 (*Trans.*, lxi., 114-148). The results are arranged in three sections.

I. The Physical and Chemical Properties of Colloidal Arsenious Sulphide.—The precipitates, which separate when arsenious sulphide is coagulated by metallic salts, are regarded as metallic derivatives of a complex hydro-sulphide formed by interchange of hydrogen for metal. Thus, $x\text{As}_2\text{S}_3 \cdot \text{H}_2\text{S} + \text{BaCl}_2 = x\text{As}_2\text{S}_3 \cdot \text{BaS} + 2\text{HCl}$.

The coagulation process for salts of uni-, bi-, and ter-valent metals is reviewed in the light of this hypothesis. Quadrivalent metals, such as platinum and zirconium, are found to be non-coagulants of arsenious sulphide in dilute solution.

The aggregation and de-aggregation phenomena of arsenious sulphide have been studied microscopically.

II. The Physical and Chemical Properties of Colloidal Ferric Hydroxide.—Various "grades" of colloidal ferric hydroxide have been prepared by dialysis. The physical

and chemical properties of certain of these solutions and the coagulation phenomena of the colloidal hydroxychloride have been studied by methods similar to those applied in the investigation on arsenious sulphide.

III. Dyeing, a Phase of Coagulation.—The "substantive dyeing" of colloidal ferric hydroxide and arsenious sulphide by methyl-violet and aniline-blue is shown to exhibit phenomena which are precisely analogous to those occurring when these colloids are coagulated by metallic salts.

186. "The Influence of very Strong Electromagnetic Fields on the Spark Spectra of Ruthenium, Rhodium, and Palladium." By JOHN EDWARD PURVIS.

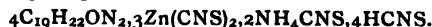
The experiments were made with a 21-foot concave grating spectroscope. The spark passed between electrodes of the metals which were firmly held between the poles of a magnet. The strength of the field between the poles of the magnet was 40,000 units with a current of 21 amperes. The nature of the vibrations was analysed by a calcite prism. The general results showed that (1) most of the lines are divided into triplets, and that there is a periodic or rhythmic change in the directions of the vibrations of the constituents of the triplets. (2) Some lines become quadruplets, and within certain definite regions of the spectrum their constituents also change the directions of their vibrations. (3) Other lines become doublets. (Only a very few lines are not affected when vibrating in the magnetic field). (4) The inner member of the triplets is usually the strongest; but this is not always the case. The two outer members of a triplet may be stronger than the inner one; and all three are sometimes equally strong. (5) The strongest spectral lines are not the most widely separated when vibrating in the field. Weak lines are usually more widely separated than strong ones. (6) The decrease in the width of the triplets does not proceed *pari passu* from the less refrangible to the more refrangible end of the spectrum.

187. "A Volumetric Method of Estimating the Cinchona Alkaloids by means of their Double Thiocyanates." By PHILIP WILFRED ROBERTSON.

Skey has pointed out that many alkaloids give precipitates with ammonium thiocyanate in the presence of a zinc or mercury salt. Many other metals act in a similar manner; zinc, however, forms the most insoluble precipitates. The alkaloids most sensitive to this reaction are quinine and the cinchona alkaloids. Thus in the presence of excess of zinc sulphate and ammonium thiocyanate, one part of quinine gives a distinct turbidity in 50,000 parts of water.

These precipitates prove to be double salts of considerable complexity, as is the case with the compounds of many alkaloids, more especially quinine and its allies.

Thus cinchonine ammonium zinc thiocyanate has the following composition:—



This formula corresponds closely with that of herapathite or iodoquinine sulphate,—



Notwithstanding the complexity of these double salts, the determination of the amount of thiocyanate removed from solution by the alkaloids forms an accurate and speedy volumetric method of estimating quinine in the commercial drugs and in the assay of the crude cinchona bark.

188. "The Osmotic Pressure of Sugar Solutions in Mixtures of Alcohol and Water." By PERCIVAL SMITH BARLOW.

Some experiments have been made with copper ferrocyanide membranes and solutions of sugar in a mixed solvent of alcohol and water, which confirmed Tammann's observation that an osmotic current cannot be obtained with these membranes and alcohol. The author's experiments were spread over a considerable time, in some cases months being allowed to elapse, so that every opportunity

might be afforded for the pressure to show itself. For membranes permeable to water only, the van't Hoff value of the osmotic pressure is very much diminished by the presence of the alcohol, but no idea has been obtained as yet of any relation between the amounts of alcohol present and the amount of the reduction in the pressures; below a certain strength of sugar solution there is no direct evidence of osmotic pressure, the alcohol present quite overshadowing the effect of the sugar. There are indications that the membrane is rendered permeable to the sugar by the presence of alcohol. For a membrane permeable to the alcohol only, the pressure set up is very much less than above, and is produced extremely slowly. Whatever molecular aggregates are formed in connection with the sugar, it seems that the alcohol molecule takes much less part in them than the water molecules.

Research Fund.

A Meeting of the Research Fund Committee will be held in December next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, December 11th, 1905.

PHYSICAL SOCIETY.

Ordinary Meeting, November 24th, 1905.

Prof. J. H. POYNTING, F.R.S., President, in the Chair.

A PAPER ON "The Dielectric Strength of Air" was read by Mr. A. RUSSELL.

The dielectric strength of air, at a given barometric pressure, is generally deduced from the results of experiments made on the disruptive voltages between equal metal electrodes at given distances apart. It is assumed that the electric field surrounding the two electrodes just before the disruptive discharge takes place is similar to that round the electrodes at low voltages. Schuster has shown that this assumption is untenable. The author has found that in certain cases the dielectric has broken down before the final discharge takes place. Hence the boundaries of the Faraday tubes are no longer the surfaces of the metal electrodes, but the boundary of that part of the dielectric surrounding the two electrodes which has ceased to insulate and has become a conductor. It is known that for various gases there are certain minimum sparking potential-differences between the electrodes. The electrostatic equations fail to take this into account. The author therefore makes the assumption that for distances apart greater than about a millimetre when the disruptive voltage is V kilovolts the effective P.D. between the ends of the Faraday tube which is subject to the maximum stress is $V - \epsilon$, where ϵ is the minimum sparking voltage. Applying formulæ which he has deduced, using this assumption, to tests of Heydweiller, Steinmetz, Algermissen, &c., the author finds that they agree in making the dielectric strength of air 38 kilovolts per c.m. approximately. A knowledge of this quantity enables us to find not only the disruptive voltages between electrodes of many geometrical shapes, but it also enables us to find the "critical" pressure for overhead electric-power transmission at high pressures. The author gives a complete proof by Kelvin's method of images of the Kirchhoff series-formula, and shows how its numerical value can be readily found both by ordinary algebra and by elliptic function series.

Dr. H. A. WILSON expressed his interest in the author's explanation of the brush discharge and the formation of coronas. There were, however, one or two points in the paper which required some alteration. The author stated that according to Strutt the minimum sparking potential-difference was 767 volts when the barometric pressure was 72.4 c.m. The pressure in Strutt's experiments was, however, 72.4 m.m. When the distance between the electrodes was not too small it was known that the sparking P.D. could be expressed as $V = a + \beta d$, where d

was the distance between the electrodes and a and β were constants. This constant β the author had called the dielectric strength of air, but he did not think he was justified in doing so.

The CHAIRMAN, referring to Table V. in the paper, asked if the rise in value of the dielectric strength as the distance apart of the electrodes increased was due to the formation of coronas.

Mr. RUSSELL, in reply, thanked Dr. Wilson for pointing out that in the paper the atmospheric pressures at which Mr. Strutt had obtained his results were quoted in c.m. instead of m.m. Mr. Strutt had shown that the P.D. between the cathode and the negative glow was 341 volts whatever the atmospheric pressure. We were therefore quite justified in assuming that at ordinary pressures the electric pressure on the Faraday tube subject to the maximum stress is $V - \epsilon$, where ϵ is greater than 341. The experimental results analysed in the paper indicate that ϵ is 0.8 of a kilovolt. In answer to Prof. Poynting, he stated that the slight rise in the values of the dielectric strength in Table V. was probably due to the potentials of the electrodes not being V and zero at the instant of discharge.

A paper by Dr. H. A. WILSON and Mr. E. GOLD, "On the Electrical Conductivity of Flames for Rapidly Alternating Currents," was read by Dr. WILSON.

This paper contains an account of a series of experiments on the electrical conductivity of a Bunsen flame containing various alkali-salt vapours for alternating currents with frequencies from 7×10^4 to 11×10^4 alternations per second. The conductivity was measured between two platinum electrodes immersed in the flame, and the variation of the conductivity with the amount of salt present and with the nature of the salt was investigated. The variation of the conductivity with the frequency of alternation, the maximum E.M.F., and the distance between the electrodes was also examined. The results obtained enable a comparison to be made between the conductivities of various alkali-salt vapours for alternating currents and their conductivities for steady currents as previously determined. The conductivity was measured by means of a Wheatstone's Bridge, three arms of which consisted of small air-condensers and the fourth of the electrodes in the flame. One of the condensers could be adjusted until a balance was obtained. The following is a summary of the results:—1. For rapidly alternating currents a flame containing an alkali-salt vapour behaves like an insulating medium of high specific inductive capacity. 2. The conductivity of different alkali-salt vapours in a flame for rapidly alternating current as measured by the apparent capacity of platinum electrodes immersed in the flame, varies as the square root of the conductivity of the same salt vapours for steady currents. This result confirms the view that the negative ions from all salts have the same velocity. 3. The apparent capacity varies nearly inversely as the square root of the maximum applied P.D. 4. The apparent capacity is nearly independent of the number of alternations per second. 5. The apparent capacity is nearly independent of the distance between the electrodes. 6. The results 1 to 5 are in agreement with the ionic theory of the conductivity of the flame for rapidly alternating currents when the velocity of the positive ions and the inertia and viscous resistance to the motion of the negative ions are neglected in comparison with the effects due to the number of ions per c.c. 7. The apparent capacity per sq. c.m. area of the electrodes is equal to $\sqrt{ne/8\pi V_0}$, where n is the number of positive ions per c.c., e the charge on one ion, and V_0 the maximum applied P.D. 8. Not more than molecule in ten of salt molecules is ionised at any instant, but each molecule is probably ionised and re-combines several million times per second. 9. The steady currents observed through salt vapours in flames are very far from the maximum possible currents corresponding to the number of ions produced per second.

Mr. W. DUDELL expressed his interest in the method of measurement and referred to the fact that although the paper was entitled "The Electrical Conductivity of

Flames." The Authors had not measured conductivities, but a complex quantity which was equivalent to a resistance shunted with a condenser. He drew attention to one of the tables given in the paper in which numbers referred to as constant varied by over 50 per cent.

Dr. WILSON said the quantity which they had measured was the apparent capacity of the electrodes.

A paper "On the Lateral Vibrations of Loaded and Unloaded Bars" was read by Mr. J. MORROW.

This is a continuation of the work previously communicated by the author on the "Vibration of Bars of Uniform and Varying Sectional Area." By means of a method of continuous approximation, the elastic displacement curves and the frequency of the lateral vibrations of bars can be determined to any required degree of accuracy. The method is first applied to some cases of unloaded bars, and also to massless bars carrying concentrated loads. The paper then deals with the principal problems of loaded bars which are themselves of appreciable mass. The equations in their general forms are cumbersome, but for a given position of the concentrated load and for a given ratio of the mass of the load to that of the bar the expressions for the frequency become very simple. In order to reduce the results to a form available for practical use, the numerical constants in these expressions have been worked out for the different positions of the load and for ratios of mass of load to that of bar ranging from 0 to 1.0. In the last section of the paper the method is applied to find the corrections due to the rotatory inertia of the masses and of the sections of the bar, and a comparison is given with the methods employed by Lord Rayleigh and Dr. Chree for similar purposes.

CORRESPONDENCE

ESTIMATING THE CONSTITUENTS OF DOLOMITE.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, September 8th, 1905 (vol. xcii., p. 108) Mr. Nicholas Knight criticises the method of estimating the constituents of dolomite, as described in our text-book on Quantitative Analysis.

The method there described is not intended for the use of industrial analysts, but is given as an example for students who are commencing the analysis of minerals. It is therefore a typical analysis, and as such we deem it should be exact.

As some of the estimations are described for the first time in this analysis, and are subsequently frequently referred to, precautions are suggested which would be unnecessary in a commercial analysis of a limestone.

Below are appended reasons why these methods are chosen.

1. *Silica*.—In siliceous limestones an appreciable quantity of silica goes into solution when the substance is dissolved in hydrochloric acid, hence in accurate analysis it is necessary to evaporate to dryness and heat the residue to 150° C.

2. *Iron Oxide and Alumina*.—If small quantities of ferric and aluminium hydroxides are precipitated in the presence of much calcium salt, we have found that the first precipitation with AmOH always carries down some calcium.

In the analysis given below, in which the ordinary laboratory reagents were used, 0.09 per cent of lime was found to be thus co-precipitated. In order to make sure that its precipitation was not due to the ammonium hydrate having been slightly carbonated, some freshly prepared ammonia solution was made by passing ammonia gas into recently boiled distilled water. This reagent was used to precipitate the hydroxides of iron and aluminium, and the precipitate was filtered and washed. It was then dissolved in hydrochloric acid, precipitated again with the fresh am-

monia solution, and filtered off. The filtrate was found to give a distinct precipitate with ammonium oxalate solution, showing that calcium had been originally precipitated with the ferric and aluminium hydroxides.

3. *Magnesia*.—If great care is taken that ammonium salts are present in small quantity only, it is not absolutely necessary to ignite before precipitating the magnesium as double phosphate. But since students frequently add ammonium salts freely, and in the method suggested by us powdered ammonium oxalate is added to ensure the rapid formation of a granular precipitate, it is necessary to ignite before estimating the magnesium.

In an estimation carried out under the above conditions 14.62 per cent of MgO was found after ignition, but only 14.44 was found if the ignition was omitted.

Recent analyses of a dolomite made in one of our laboratories serve to indicate the different results obtained by the method suggested by us (A) and that by Mr. Nicholas Knight (B).

	Method A.	Method B.
Fe ₂ O ₃ + Al ₂ O ₃	1.35	1.43
CaO	37.04	37.03
Additional CaO brought down with		
Al ₂ O ₃ and Fe ₂ O ₃	0.09	—
MgO	14.62	14.58

The CaO in Method A was obtained after a single precipitation of the ferric and aluminium hydroxides by ammonia solution.

It will be seen that after a second precipitation of these oxides a further quantity of calcium was obtained from the filtrate. This amount almost exactly makes good the difference in the percentages of Fe₂O₃ + Al₂O₃ obtained by the two methods.

The difference in the percentages of MgO is not so important.—We are, &c.,

FRANK CLOWES.
J. B. COLEMAN.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

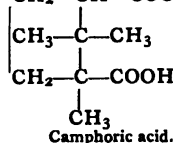
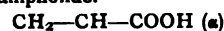
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 18, October 30, 1905.

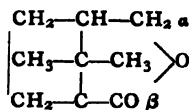
This number contains no chemical matter.

No. 19, November 6, 1905.

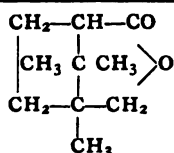
On the Mixed Function Derivatives of Dextro-camphoric Acid, and on the β -Campholide.—A. Haller and G. Blanc.—In a previous communication, one of the authors showed that camphoric anhydride reduced in alcohol by sodium amalgam generates a lactone, α -campholide, reproduced later by MM. Baeyer and Williger by treating camphor with potassium sulphate and sulphuric acid, and quite recently by reduction of the α -methyl acid camphorate. This lactone can be converted into nitrile by potassium cyanide, then into homo-camphoric acid, the lead salt of which, on calcining, gives camphor, with its original properties. These reactions show that it is easy to pass from camphoric acid to camphor. But in camphoric acid the bonds of union of the two carboxyl groups are not identical, so that it is possible to imagine a second campholide, which they call β -campholide.



Camphoric acid.



α -Campholide.

 β -Campholide.

This compound, treated in the same way as the α -campholide, should give a nitrile, a homocamphoric acid, and, finally, a new camphor isomeric with the corresponding derivatives of the α -compound. Unsuccessful attempts to prepare this β -lactone had already been made in 1896. The authors then experimented with β -methyl acid camphorate, which is formed by saponification of neutral methyl camphorate with alcoholic potash. They then reduced it with sodium and absolute alcohol, following a method which resulted in the transformation of isolauroic acid into the corresponding alcohol. After the preparation of the

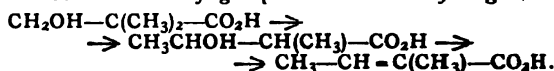
β -chloride, $\text{C}_8\text{H}_{14}\text{COCl}$, the authors passed readily to the methyl- β -camphoramate, the β -phenylhydrazine of the α -methyl compound, and propose to return later to the preparation of many mixed derivatives of camphoric acid from this chloride. From the α -chloride, $\text{C}_8\text{H}_{14}\text{COCl}$, they prepared the β -methyl- α -camphoramate, crystallising in more beautiful crystals than its isomer above, but possessing a smaller rotatory power. The anilide, β -toluide, and phenylhydrazide ethers could not be obtained in crystalline form. The β -campholide was prepared by reducing a solution of 50 grms. of β -methyl acid camphorate in 350 grms. of alcohol by 50 grms. of sodium. The campholide was extracted with ether and purified by crystallisation. A kilogram. of β -acid ether only gave 26 grms. of lactone. The β -campholide crystallises in a mixture of ether and petroleum ether, the crystals melting at $218-220^\circ$ in a closed tube. It is very soluble in alcohol and ether in hot soda, but is re-precipitated by mineral acids. The authors tried to pass this β -campholide through the same changes as the α -compound, in order to interchange the CO and CH_2 groups, but with little success. They arrive at the following conclusions:—

1. That it is possible to obtain β -campholide isomeric with that prepared by one of them from the reduction of camphoric anhydride, but that this new lactone does not easily lend itself to double decomposition with potassium cyanide. 2. That the α - and β -camphoric acid ethers (ortho and allo) supply corresponding ether chlorides capable of giving molecules of mixed function. Even if they have not succeeded in attaining their end, the authors maintain that their researches bring into prominence the great functional differences shown by certain groupings according to the molecule to which they are attached. In the β -campholide, as in the β -camphoric acid ethers, the functional groups which resist the action of reagents are both united to the

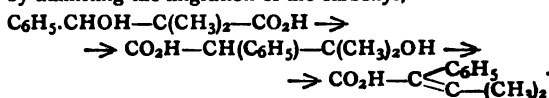
carbon —C— , whilst in their α -isomers the same groupings are attached to the carbon —C— . It seems that the presence of one atom of hydrogen united to the carbon which is attached to the group CO_2R or $\text{CH}_2>\text{O}$ favours a reaction.

Molecular Transpositions and Migration of the Carboxyl Group in the Dehydration of certain Hydroxy Acids.—E. E. Blaise and A. Courtot.—It is well known that β -hydroxy acids dehydrate easily, giving non-saturated β -acids. But when the α -carbon is dialcylated this mode of dehydration is no longer possible up to the present. Acting with phosphoric anhydride on the ethers of the dimethylhydracrylic acids, the authors have obtained ethers of non-saturated β -acids. Particularly have they prepared dimethylvinylacetic acid, the constitu-

tion of which they previously established. The same method gave dimethylpropenylacetic, dimethylisopropenylacetic, and dimethylphenylvinylacetic acids, of which more anon. From the point of view of dehydration, the most interesting of the ethers are those not possessing any hydrogen united to the γ -carbon, or those in which the alcoholic function being primary—the chain is limited to the β -carbon. The authors find that, on dehydrating oxypivalic acid, a hemipolyactide is obtained; but by acting on the ethylic ether the dehydration is accompanied by a transposition, and a mixture of tiglate and angelate of ethyl is obtained. The reaction necessitates a permutation between a methyl-group and an atom of hydrogen,—



The formation of dimethylatropic acid by the dehydration of dimethylphenylhydracrylic acid can only be explained by admitting the migration of the carboxyl,—



This interesting reaction, so far as the authors are aware, is the first observed example of the migration of the carboxyl group in a synthetical molecule. It shows that this migration may be normal in certain transformations on natural substances, as, for instance, the conversion of camphoric acid into isolauroic acid.

MISCELLANEOUS.

Messrs. F. Wiggins and Sons, Mica Merchants, announce that their only address now is 102/103, Minories, London, E.C.

MEETINGS FOR THE WEEK.

- MONDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "Measurement of High Frequency Currents and Electric Waves," by Dr. J. A. Fleming, F.R.S.
— Society of Chemical Industry, 8. "Notes on Guttapercha and Balata," by W. A. Casperl. "Determination of Zinc in Zinc-aluminum Alloys," by R. Seligman and F. J. Willott. "Distilled Water Supply for a Works Laboratories," by R. Seligman. "Estimation of Naphthalene in Coal-gas," by C. J. Dickinson-Gair. "Salts of the Alkaloid Cinchonamine," by B. F. Howard and F. Perry.
— Royal Institution, 5. General Monthly Meeting.
- WEDNESDAY, 6th.—Society of Arts, 8. "The Manufacture of Sugar from British-grown Beet," by Sigmund Stels.
— Society of Public Analysts, 8.
- THURSDAY, 7th.—Society of Arts, 4.30. "The Partition of Bengal," by Sir James A. Bourdillon.
— Chemical, 8.30. "The Constitution of Nitrites—Part I. Two varieties of Silver Nitrite," by F. C. Rây and A. C. Ganguli. "The Products of Heating Silver Nitrite," by E. Divers. "Ethyl Piperonyl Acetate," by W. H. Perkin, jun., and R. Robinson. "Contribution to the Chemistry of Saccharin," by F. D. Chattaway. "Action of Heat on α -Hydroxycarboxylic Acids" (Part II.), by H. R. Le Sueur. "Studies on Optically Active Carbimides—Part II. The Reactions between 1-Menthylcarbimide and Alcohols," by R. H. Pickard, W. O. Littlebury, and A. Neville. "Action of Ultra-violet Light on Moist and Dried Mixtures of Carbon Monoxide and Oxygen," by S. Chadwick, J. E. Ramsbottom, and D. L. Chapman.

GOVERNMENT GRANT to defray the expenses of Scientific Investigations. Applications for the year 1906 must be received at the Offices of the Royal Society not later than JANUARY 31st next, and must be made upon printed forms to be obtained from the Clerk to the Government Grant Committee, Royal Society, Burlington House, London, W.

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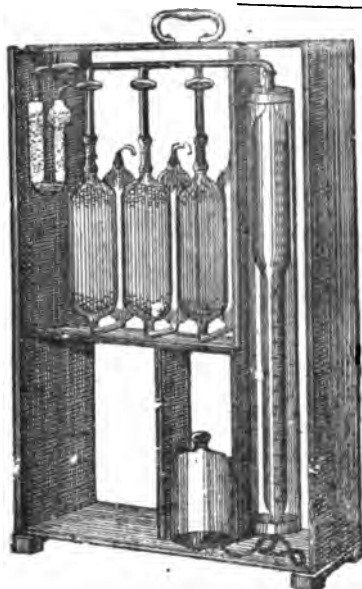
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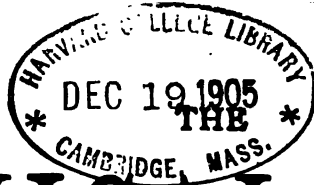
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Chem Lab

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE

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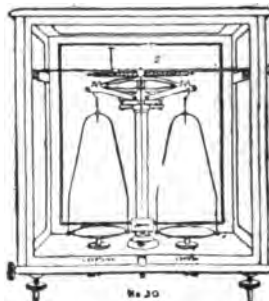
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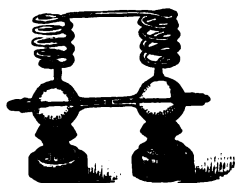
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THE CHEMICAL NEWS.

VOL. XCII., No. 2402.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A. GUYE

In different ways, which, however, agree in their results, the conclusion is to-day arrived at that the atomic weight of nitrogen, as found by Stas, is inaccurate. The error is $1/467$ if one refers to the value $N = 14.04$ of the International Table for 1905; it is $1/311$ if one takes the number assigned (1882) by the illustrious Belgian chemist, $N = 14.055$. In other words, the probable value of the atomic weight of nitrogen is $N = 14.01$.

In the first place it may be asked how, since the celebrated work of Stas, published in 1860 and 1865, chemists have been able to content themselves with a value containing so considerable an error without its having been discovered; it seems particularly strange that the numberless nitrogen estimations carried on yearly in the different departments in which this element plays so important a part—such as it plays in inorganic or organic chemistry, in rural economy, in the explosives industry, &c.—have not served to make the error apparent. I see only one plausible explanation; it is that the great majority of chemists have continued to make their calculations with the round number $N = 14.00$, adopted about 1843, as a result of Marignac's work, this number differing from the correct number by $1/1400$.

However that may be, it is evidently not possible to abandon the results of an experimenter so eminent as Stas without being absolutely sure that they are erroneous. This explains and justifies the wisdom of the International Committee on Atomic Weights, which certainly cannot be reproached for having so far retained the value $N = 14.04$. But to-day, in spite of the great and legitimate admiration which the labours of Stas everywhere inspire and will long continue to inspire—and I am of the number of his admirers, of those in particular who cherish a remembrance of the kind reception of the Master in his laboratory in Brussels—the moment has come in which one should have the courage to break with the past and to recognise the error committed. The careful examination of the question, the substance of the review of research upon the subject, demonstrate:—

1. That the classical gravimetric methods pursued by Stas, by his predecessors, or by his successors, are not capable of sufficient accuracy to guarantee the second decimal of the atomic weight of nitrogen.
2. That the new methods of a physico-chemical nature allow, on the other hand, of attaining to this accuracy, and point to the value $N = 14.01$.
3. That the new gravimetric methods, more rational and more accurate than those previously followed, lead to results which confirm the value of the atomic weight of nitrogen obtained by the physico-chemical methods.

It is these three classes of considerations that I desire now to investigate with you.

But, to begin with, it is desirable to say a few words on the history of the question. It was first in 1805 that serious doubt was cast by Lord Rayleigh and Sir William Ramsay upon the atomic weight of nitrogen. Having determined with great accuracy the density of chemical nitrogen, these scientists estimated this density, referred to that of oxygen ($O = 16$), to be 14.003 ; for atmospheric

nitrogen, mixed with argon, this ratio is 14.07 , coinciding nearly with Stas's number, 14.055 or 14.06 , a singular fact but not unique in the history of science, which has certainly contributed towards giving a false confidence in the accuracy of this number.

Shortly afterwards M. Leduc, at the conclusion of his beautiful researches upon gases, was led in 1897 to substitute for the value $N = 14.075$, which he had proposed in 1894 for the atomic weight of nitrogen, the number $N = 14.005$.

It is this same value $N = 14.005$ that D. Berthelot finally arrived at in his remarkable memoir on the method of density-limits (1898), based principally on the observations of MM. Leduc and Sacerdote.

Finally, in 1900, in the course of researches on the constants of the equation of Van der Waals, which have obliged us to choose as exact a value as possible for the atomic weight of nitrogen, Friderich and I adopted the number $N = 14.005$, relying principally on the ratio of the densities of nitrogen and hydrogen, corrected to the mean of the compressibility experiments by Regnault.

While these physico-chemical experiments were being carried on, certain revisions by gravimetric methods were undertaken, but without leading to any conclusive results. This at least is the impression gained by reading reviews by Richards, a scientist particularly competent to judge of these matters, and from whom I borrow the following summary:—

TABLE I.—Methods.

	N.
Ratio—HCl : NH ₃ (Thomsen, 1894)	14.021
Ratio—Ag : AgNO ₃ (Hardin, 1896)	14.01
Ratios— { KNO ₃ : KCl } (Hibbs, 1896) ..	14.01
{ NaNO ₃ : NaCl }	
Ratio—AgCN : Ag (Dean, 1900)	14.031
Analysis—Salts of nitrous acid (Ramsay and Aston, 1903)	13.903
Ratio—Na ₂ CO ₃ : 2Na ₂ NO ₃ (Richards) ..	14.02
Ratios— { CsNO ₃ : CSO ₃ } (Richards & Archibald, 1904) ..	14.037 to 14.040
{ KNO ₃ : KO ₂ }	

The latest experiments of Richards and Archibald in particular were not of the nature to dissipate the discordance between the physico-chemical results, on the one hand, and the gravimetric results on the other; this in effect was a confirmation of the international atomic weight $N = 14.04$.

In the presence of such a want of agreement, the more profound study of the question imposed itself afresh: either the classic methods or the physico-chemical are in error; one of the contradictory results should be discarded.

With the view to endeavour to elucidate this problem, various researches of an experimental or theoretic nature were undertaken in my laboratory, from the years 1901 to 1902, the object of the one being to determine different points connected with the physico-chemical methods, the others to lay the foundation of new gravimetric methods more rational than those employed hitherto.

The work entailed by the execution of the programme thus traced was considerable; it would not have been possible to bring it to a satisfactory conclusion in so short a time without the valuable and enlightened co-operation of friends and former pupils; my assistant, Dr. A. Jaquerod, as well as Drs. St. Bogdan, C. Davila, L. Demolis, E. Mallet, L. Perrot, A. Pintza, and O. Schener, have kindly assisted in the different sections of these researches.

It is therefore of the sum of this work that I shall speak, and it is from the discussion of their results, a discussion frequently general, that the three fundamental conclusions I just now formulated have arisen.

I am thus brought back to my subject; it only remains for me to ask your indulgence for the use of numerical tables which I am obliged to lay before you in order to make clear to you the conviction gained after a personal effort of many years.

(To be continued).

* From the *Bulletin de la Société Chimique de Paris*, 1905.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

(Continued from p. 254).

Reactions of the Double Fluorides of Columbium, Titanium, Tantalum, Tin, and Tungsten with various Reagents in Concentrated Sulphuric Acid.

A SMALL amount of the reagent was dissolved in eight to ten drops of concentrated sulphuric acid on a glazed porcelain surface, and the crystalline double fluoride introduced into this acid solution. In most cases the colour was destroyed upon diluting with water. No colour was imparted to tin solutions by any of the reagents which appear in the accompanying table.

Reagent.	Ta.	Cb.	Ti.	W.
Codeine	No colour.	No colour.	Faint pink, may be due to morphine.	Light brown; on standing, trace purple.
Morphine . . .	Faint yellow.	—	Red to brown, very delicate.	Grey - brown, becoming purple; H ₂ O ppt.
Resorcinol ..	No colour.	No colour.	Red-brown, fairly delicate.	No colour.
Naphthol (β) ..	"	Faint yellow brown.	Coffee brown, very delicate.	Brown, becoming dark blue.
Naphthol (α) ..	"	Faint brown.	Green to dark greenish brown.	Deep blue, very delicate.
Pyrogallol ..	"	Yellow to light brown.	Dull dark red.	Deep red to brown to dirty blue.
Salicylic acid ..	"	Very faint yellow.	Deep red.	Reddish yellow.
Cinchonidine ..	"	No colour.	No colour.	On standing, a slight purple.
Apomorphia ..	"	Yellow brown.	Light red-brown.	Purple to brown to green and blue.
Narceine.. ..	"	Brownish yellow.	Brown.	Dirty dark green.
Bebeerina . . .	"	No colour.	Clear brown.	Dark brown to green.
Narcotina . . .	"	Yellow.	Brown.	Light brown to green.

Strychnia, quinidia, cinchonidine, and atropia gave no colour with any of the elements tested. Narceine and bebeerina alone in sulphuric acid gave a considerable colour, and with them the amount of reagent must be very small, or it will obscure any change produced by the addition of the double fluoride. In this connection it is of interest to note that Levy (*Comptes Rendus*, ciii., 1074, 1195) studied the colours produced by the phenol-like bodies, dissolved in concentrated sulphuric acid, when brought in contact with the oxides of titanium, tin, tantalum, columbium, and other elements, with the following results:—Columbium could be tested for in the presence of all the others by using codeine, as it gave a pink colour, while titanium yielded no colour, and tantalum but a faint green. Titanium could be tested for by using morphine, with which it gave a carmine colour, columbium no colour, and tantalum a yellow colour passing into brown. Tantalum with resorcinol gave a dirty green colour, changing to amethyst and rose, while titanium yielded a flesh-red colour, going to chocolate-brown, and columbium a yellowish tint. None of the results were duplicated save the morphine test for titanium, which proved exceedingly delicate, yet to have the colour show definitely in columbium the latter must contain 0.5 per cent of TiO₂. Codeine gave no colour with columbium, nor did resorcinol with tantalum, therefore Levy could not have had pure material for his tests.

In our use of these reagents we failed to find satisfactory tests, except in the case of morphine for titanium. None answered for columbium in the presence of titanium, or for tantalum in the presence of columbium. Resorcinol proved to be a fairly delicate test for titanium; it gave no colour with columbium, tantalum, or tungsten.

Action of Hydrochloric Acid Gas on Ignited Columbic Oxide.

0.25 grm. of ignited columbic oxide was completely volatilised in three hours in a current of dry hydrochloric

acid gas. It volatilised as a white powder, with no indication of reduction by change of colour. The compound formed adhered to the walls of the glass tube, was insoluble in oxalic acid, and only very slowly soluble in concentrated sulphuric acid, requiring long boiling to dissolve a thin layer. It contained hydrochloric acid, as was shown by washing with ammonium hydroxide and testing the washings with silver nitrate and nitric acid. It would be very difficult to collect in a form convenient for analysis; yet this should be done, as the body evidently contains no water, as is given in the formula of a similar body obtained by Smith and Maas (*Zeit. Anorg. Chem.*, vii., 96) by passing moist hydrochloric acid gas over the hydrated oxide. It is undoubtedly analogous to the body obtained on heating molybdic acid in hydrochloric acid gas, namely, MoO₃.2HCl. It is probably Cb₂O₅.xHCl.

Action of Sulphuric Acid on the Hydrates of Columbium and Titanium after Precipitation by Ammonium Hydroxide from Solutions of their Double Fluorides.

The method used was to precipitate the hydrates from a weighed amount of the double fluorides, filter, and wash as thoroughly as possible; then transfer to a weighed platinum dish, re-weigh (the difference being water), after which a weighed amount of sulphuric acid of definite specific gravity was added and allowed to stand in contact with the hydrates for a definite time. The portion insoluble was filtered off, and the amount of oxide going into solution determined by precipitation with ammonium hydroxide, igniting, and weighing. The amount of titanium in the oxide which went into solution was determined colorimetrically.

In making these trials columbium oxyfluoride was used in which the titanium oxide, as compared with the columbium oxide, was 0.00095 grm. TiO₂, or 0.41 per cent. The specific gravity of the sulphuric acid used was 1.145.

Experiments.

1. One grm. of K₂TiF₆, containing 0.3330 grm. of TiO₂, was used to obtain the hydrate. The latter was treated with 40 c.c. of water and 70 grms. of sulphuric acid. It dissolved completely in fifteen minutes.

2. 0.4450 grm. of columbic oxide, in the form of hydrate was treated with 40 grms. of water and 108 grms. of sulphuric acid for one hour. Only a slight precipitate was obtained with ammonium hydroxide in the filtrate. It was not weighed, but contained 0.00032 grm. of TiO₂, or 0.07 per cent of the total oxide taken, or one-sixth of the total TiO₂ present.

3. Columbic hydrate, containing 0.4450 grm. of oxide, was treated with 60 grms. of water and 123 grms. of sulphuric acid for four hours. The portion which dissolved equalled 0.0060 grm. = 1.33 per cent, and contained 0.000424 grm. of TiO₂, or 7 per cent of the oxide dissolved, and about one-fourth of the total titanium present.

4. The hydrate from 3 grms. of columbium oxyfluoride, equivalent to 1.35 grms. of oxide, was allowed to stand in

* *Proceedings of the American Philosophical Society*, 1905, xliv., p. 177.

contact with 50 grms. of water and 100 grms. of sulphuric acid for seventeen hours. The acid solution showed 0.0236 grm. of oxide = 1.75 per cent, containing 0.000954 grm. TiO_2 = 4 per cent of oxide dissolved, or 17 per cent of the total TiO_2 present.

5. Hydrate containing 0.445 grm. of oxide, when treated with 57 grms. of water and 85 grms. of H_2SO_4 (specific gravity = 1.435) for forty-five hours, showed in solution 0.0500 grm. = 11.1 per cent, containing 0.0008 grm. TiO_2 = 1.6 per cent of the oxide dissolved, or 43 per cent of the total TiO_2 present.

Known amounts of the two hydrates were next treated together as in the following experiments:—

6. 0.2816 grm. of K_2TiF_6 , containing 0.0939 grm. of TiO_2 , and 0.5078 grm. of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, containing 0.2255 grm. C_2O_3 , were treated with 50 grms. of water and 15 grms. of sulphuric acid (specific gravity = 1.435) for four hours. The amount of oxide remaining insoluble was only 0.07 grm. It was not examined as to its titanium content.

7. The hydrate from 0.2420 grm. K_2TiF_6 , containing 0.0807 grm. TiO_2 , and that from 0.3454 grm. of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, containing 0.1537 grm. of C_2O_3 , were covered with 70 grms. of water and 5 grms. of sulphuric acid of specific gravity 1.435. The amount of oxide in solution after four hours was 0.0800 grm., corresponding well with the weight of the oxide of titanium present, but the insoluble portion was found to contain 0.0350 grm. of TiO_2 , determined colorimetrically; so that only about one-half of the titanium hydrate had been dissolved out, while nearly as much columbium hydrate had gone into solution. The acid used would not have dissolved any columbium hydrate had it been free from titanium hydrate; further, it would have dissolved out all of the titanium hydrate had it not been mixed with the columbium hydrate. It may therefore be concluded that this method of separation is worthless. It remains to be seen how haloid acids would act.

The Chromotropic Acid Test for Titanium.

Geisow (Dissertation, 1902) observed that the colour developed by chromotropic acid with titanium solutions offered a very delicate test for that element. In concentrated solution it gives a deep red, in dilute solutions a pink colour. The colour-giving compound was isolated by Geisow, and found to have the following composition:—One molecule of chromotropic acid to four of TiO_2 and nine of H_2O .

As it was most important to find some means of estimating the amount of titanium in columbium we were induced to study this reaction of Geisow, using solutions of titanate hydrate in oxalic, sulphuric, and hydrochloric acids.

Solutions Used.

- A. 0.53 grm. of TiO_2 dissolved in 3.42 grms. of oxalic acid and diluted to 500 c.c. 1 c.c. = 0.00106 grm. of TiO_2 , and contained 0.00684 grm. of oxalic acid.
- B. Ten c.c. of A diluted to 100 c.c. 1 c.c. = 0.000106 TiO_2 .
- C. Ten c.c. of B diluted to 100 c.c. 1 c.c. = 0.0000106 TiO_2 .
- D. Ten grms. of oxalic acid in 100 c.c. 1 c.c. = 0.1 grm. of oxalic acid.
- E. One grm. of chromotropic acid in 100 c.c.

50 c.c. Nessler tubes, 1 inch in diameter, were used for all of the tests.

0.5 c.c. of E in 50 c.c. of water gave a mere trace of colour, for which reason the solution to be tested was always compared with another tube containing the same amount of chromotropic acid, thus making allowance for the slight colour given by the solution of that reagent.

0.15 c.c. of C gave a faint pink colour when added to 50 c.c. of water containing 0.5 c.c. of E; 0.00000159 grm. of TiO_2 in 50 c.c. of water gave a change of colour; 0.3 c.c. of the same solution gave a very distinct colouration, or 0.00000318 grm. of TiO_2 in 50 c.c. More than 1 c.c. of the chromotropic acid gave so much colour as to interfere with the delicacy of the test.

(To be continued.)

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Duddell Twisted Strip Ammeter.—A very sensitive instrument for measuring direct or alternating current. The mechanical period is very short, so that it is able to follow currents which vary over a small range as rapidly as one or two cycles per second. This instrument is most useful for observing the quick variations of the R.M.S. voltage in supply stations produced either by cyclic irregularity of the engine or by phase-swinging between alternators, converters, &c.

Broca Galvanometer, as designed by Prof. A. Broca and modified by Dr. Harker, of the National Physical Laboratory. The suspended system consists of a pair of needles whose axis is vertical, one being so magnetised as to have a north-pointing pole in the middle, while the other is magnetised inversely. A high figure of merit is attained, and the coils are readily exchanged for others of different resistance.

Dolezalek Electrometer.—The needle is suspended by a quartz-fibre which is rendered conductive by being dipped in a calcium-chloride solution and connected to any convenient source of E.M.F.; or the needle is charged and insulated, the fibre being left dry.

Grassot Fluxmeter, with large permanent magnet for demonstration, and **Duddell Magnetic Standard**. A ballistic instrument whose suspended coil has a large moment of inertia, and in which the torsional control is appreciable, so that the retarding couple acting on the coil is proportional to its angular velocity, the magnetic field in which the coil lies being of sensibly uniform intensity. When an electromotive impulse is applied to it the coil is deflected, and comes definitely to rest in a new position, the deflection being proportional to the electromotive impulse, and independent of its time-distribution.

Cadmium Cell, H Form.—E.M.F. 1.0195 volts at 18° C.; mean temperature coefficient 0.000025 volt per centigrade degree rise. To the specification of the National Physical Laboratory.

Bridge for teaching Resistance Thermometry, with thermometer in glass tubes, and **D'Arsonval Galvanometer** simple form. An inexpensive outfit for teaching.

New Form Recording Thermo-couple, with Thermo-couple fitted with reels of spare wire in head attached to Recorder. The galvanometer-boom carries a knife-edge, which is intermittently depressed upon an inked thread, one point of which is thus brought into contact with a drum. The ordinate of the point in question is measured lengthwise of the thread, the co-ordinates of the record being rectangular.

Melloni Bench, for observing the reflection, refraction, absorption, &c., of radiant energy.

Spectrometer.—The construction is especially rigid, and the collimation axis cannot be displaced by the adjustment of the eye-piece focus.

Telescope and Scale.

Astronomical Micrometer for determining micrometrically the co-ordinates of stars upon a celestial photograph impressed with a standard réseau.

Trouton Hygrometer.—A continuous recording hygrometer designed by Prof. F. T. Trouton, F.R.S., and depending on the varying weight of flannel or other fabric when in equilibrium with air of varying humidity.

Vertical Sonometer.—Two wires can be directly loaded by weights, and the vibrating length of one can be varied and clamped without the introduction of a frictional error in the estimated load.

Perry's Apparatus for Teaching Law of Helical Springs, similar to that described in Prof. Perry's "Applied Mechanics."

Burton Levelling Stand.—A geometric gimbal construction provides for two independent levelling motions about mutually perpendicular axes, the adjustments being perfectly free and without side-shake. Either adjustment can be altered while the other is clamped.

Stands for holding apparatus, with universal clamps, and **Time Markers** (Deprez and simple double marker).

MESSRS. CROMPTON AND CO.

Electrometer, devised by Mr. W. A. Price, M.A., in which the fixed and moving members are parts of concentric spheres. The pivot is at the common centre of the spheres, and the air-gap between the fixed and moving parts is unchanged by deflection or swinging.

Electrical Pyrometer, of the thermo-electric type, for engineering measurements. The thermo-couple is of nickel and steel. The steel element is in the form of a tube down the centre of which runs an insulated nickel rod. This form of couple is used for temperatures up to 1100° C.; for a lower range of temperatures the couple is of copper and constantan. The scale of the instrument at the cool junction takes account of the temperatures of the two junctions and of the average temperature of the whole apparatus.

Set of Laboratory Standard Resistances wound with manganin and aged. The cases may be filled with petroleum when inverted, and fitted with thermometers.

MESSRS. ELLIOTT BROTHERS.

Electrical Measuring Instruments.

MESSRS. EVERETT, EDGUMBE, AND CO.

Portable Photometer, designed for low price, and for rapid testing with fair accuracy without any special precautions being taken as to exclusion of stray light, regulation of voltage, &c.

Watt-photometer—a higher class portable instrument than the last-mentioned—containing a wattmeter in the photometer case, and so arranged that the efficiency in watts per c.p. is read off on the instrument scale.

Standard Photometer, direct reading, designed for laboratory use. Includes arrangement for testing arc lamps at different angles. Errors from stray light, inequality in the two sides of the photometer, &c., are compensated for as far as possible. A combined Flicker and Trotter head is employed, so that either method may be used at will.

Ammeters and Wattmeters for taking rapid measurements of power consumed by glow-lamps.

Frequency Indicator, consisting of a number of steel tongues with different periods of vibration. These are acted upon by an electro-magnet energised by the current whose frequency is desired, and the vibration is taken up by the tongue having a period corresponding with the frequency.

MR. PETER HEELE.

Large Spectrograph fitted with optical parts made of ultra-violet glass.

Spectrograph—a smaller pattern.

Solar Spectroscope, Evershed pattern.

Large Direct-vision Spectroscope, of new design.

MESSRS. A. HILGER.

Spectroscope.—Measuring in wave-lengths direct. It is calibrated on over 200 spectrum lines, and reads accurately to within 1 Angström unit from wave-length 3888 to wave-length 7724. The length of scale on a spiral drum is about 60 inches. The instrument is of the constant deviation type.

Standard Goniometer.—Prism table reads to 30 seconds and the telescope to 1 second of arc. Fitted with reflecting prisms, so that the circle can be read by the microscope without the observer moving away from the telescope.

MARCONI'S WIRELESS TELEGRAPH CO.

Cymometer, designed by Dr. J. A. Fleming, F.R.S., for making exact measurements of wave-lengths and frequencies in wireless telegraphy, or in similar high-frequency circuits. The instrument can also be used to determine small capacities, or the inductance, within certain limits, of a high-frequency circuit.

(Demonstrations will be given with this instrument).

MESSRS. NALDER BROS. AND THOMPSON.

Portable Standard Testing Set (with ohmmeter and generator).—The special feature of this set is the electrostatic instrument.

MESSRS. NEWTON AND Co. (in the Library).

Projecting Lanterns for projecting both apparatus and slides. These are triple, rotating, with three fronts which can be fitted at will with attachments for showing slides; transparent apparatus, opaque apparatus and specimens, microscopic and polariscope objects, spectrum apparatus, &c., and by swinging the lantern round any required front can be brought into play at a moment's notice. The "Transpaque" lantern is a simple and inexpensive form of projection apparatus, which in a few minutes can be altered for direct, vertical, or opaque projection, as well as for low microscopic powers, &c.

Polariscope and Microscopic Preparations.

Induction-Coil and other X-Ray Apparatus.—The set of X-Ray and High Frequency apparatus as shown comprises all that is needed for a hospital or private experimenter.

(Demonstrations will be given at intervals).

Mr. R. W. PAUL.

Universal Pyrometers and a small electric Muffle Furnace.

Duddell-Mather Standard Wattmeters and gauze resistances.

Reflecting Galvanometer, vibrationless, with new pattern scale and Nernst lamp.

Galvanometers, of the single pivot portable type.

Electrostatic Voltmeters (reflecting) for low readings.

Paul Harris Portable Test-wire.

Potentiometer Outfit, with accessories.

Standard Resistances for laboratory work.

Nernst-Paul Lamps and Lanterns for demonstration purposes.

(The Pyrometers will be shown in action).

MESSRS. JAMES PITKIN AND Co.

Holden D'Arsonval Galvanometer.—A very sensitive instrument having two suspension strips, practically unaffected by vibration. Intended to withstand rough usage.

Electric Pyrometers.—Various forms, portable and otherwise, for use in factories.

Resistance Boxes, Standard Cells, galvanometer keys and scale stands.

Measuring Instruments — ammeters, voltmeters, recorders, and cell testers.

MESSRS. RUMNEY AND RUMNEY.

Bastian Mercury Vapour-Lamps.—Illumination of the Library by means of these lamps.

(Demonstrations will be given at intervals).

MESSRS. CARL ZEISS.

An Optical Appliance to facilitate Visual Perception of Ultra Microscopic Particles.—The apparatus consists of a projection table provided with an arc lamp, optical bench, two projection applanats, and a precision slit. The image of the source of light is projected on to the precision slit by means of one of the applanats; the second applanat then serves for the purpose of projecting an image of the slit, reduced to $\frac{1}{4}$ diameters, at a distance of about 90 m.m. from the lens. The microscope situated at the end of the optical bench, and fitted for the observation of fluids, with a water immersion objective and a special trough with quartz windows, is used upright, and the objects illuminated horizontally with a very narrow beam of light. An achromatic objective, mounted on a sole-plate with cross-slide, serves as a condenser. Either fluids or solid objects may be observed.

(Gold particles in colloidal solution will be shown with the apparatus. The particles are less in size than 10μ).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, November 16th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

DR. JULIEN DRUGMAN was formally admitted a Fellow of the Society.

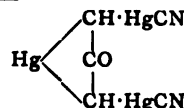
Certificates were read for the first time in favour of Messrs. William Edward Bell, 88, Monks Road, Lincoln; Thomas Harold Durrans, 1, Cornwall Terrace, Regent's Park, N.W.; Walter Hamis Glover, Ph.D., 38, Ribblesdale Road, Streatham, S.W.; William Prince Hayworth, 119, Clapton Common, London, N.E.; John Kirby Shrimpton, 22, Fountains Terrace, North Road, Ripon; Franklin Wilfred Walker, 39, Graham Road, Acton Green, W.; Richard Alfred Warren, Belle Vue, Hallow Road, Worcester; Harold Joseph Wheaton, 21, Chesterton Road, Cambridge; Herbert William Mills Willett, The Cedars, Chislehurst; Ernest Edwin Wolfe, Kinsale, Co. Cork, Ireland.

Certificates were authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Charles Anthony, jun., Town Hall, East London, Cape Colony; John Dunlop Millen, Launceston, Tasmania; Henry Rowley, Perth, Western Australia.

Of the following papers, those marked * were read:—

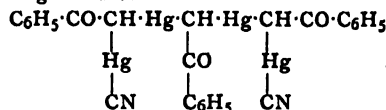
*189. "Condensation of Ketones with Mercury Cyanide." By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING-STRUTHERS.

Acetone added to a solution of mercury cyanide in aqueous caustic soda gives a white precipitate, $\text{Hg}_2\text{C}_2\text{H}_3\text{ON}_2$, insoluble in water or alcohol, which dissolves on further addition of acetone. The best yield is obtained with one molecule of acetone to not less than fifteen molecules of mercury cyanide. No precipitate at all is formed with one molecule of acetone to less than two molecules of mercury cyanide. The reaction forms a good test for acetone applicable also in presence of alcohol. The following formula represents the probable constitution of the compound:—



The same substance is formed by adding acetone to a solution of mercury cyanide and sodium ethoxide in alcohol, or sodium methoxide in methyl alcohol. The compound, which is decomposed by hydrochloric acid with liberation of acetone and hydrogen cyanide, is also decomposed by aqueous potassium cyanide with liberation of acetone. Strong sulphuric acid attacks it slowly, forming a soluble compound which is being further investigated.

Acetophenone yields a similar compound, $\text{Hg}_2\text{C}_6\text{H}_5\text{O}_2\text{N}_2$, with mercury cyanide in aqueous caustic soda; the constitution of this product may probably be represented by the following formula:—



The reactions appear to be confined to ketones containing the group CO-CH_3 ; precipitates were not obtained with diethyl ketone, benzophenone, menthone, or camphor. But ethyl acetoacetate and diphenylmethyl ketone give similar compounds. Precipitates were also obtained with ethyl malonate and ethyl isosuccinate. Aldehydes generally bring about a reduction of the mercury cyanide. Benzaldehyde and anisaldehyde give almost quantitatively their respective acids.

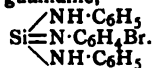
*190. "Silicon Researches. Part IX. Bromination of Silicophenylimide and -amide, and Formation of a Compound including the Group (SiN)." By JAMES EMERSON REYNOLDS.

In Part VII. of this series of papers, the author showed that the fine crystalline silicophenylamide, $\text{Si}(\text{NHC}_6\text{H}_5)_4$, described in Part V., can be made to afford silicotriphenylguanidine, and, ultimately, silicodiphenylimide, $\text{Si}(\text{NC}_6\text{H}_5)_2$. The latter is isomeric with the still unknown silicocyanamide, $\text{SiN}\cdot\text{N}(\text{C}_6\text{H}_5)_2$. The aim of the present inquiry has been to study the action of bromine directly on the di-imide, or indirectly through the silicophenylamide in the hope of forming a compound including the group SiN analogous to cyanogen.

The di-imide in the form of very fine powder was found to combine with two atomic proportions of bromine, even in the cold, when the halogen was present in benzene solution, the insoluble additive compound, $\text{Si}(\text{NC}_6\text{H}_5)_2\text{Br}_2$, being formed. When this substance was warmed with excess of bromine, also diluted with much benzene, the aniline residues were attacked and variable mixtures were obtained, which proved to be very difficult to separate. On the other hand, silicophenylamide, being easily soluble in benzene, was found to be much more suitable for the systematic study of the products of bromination.

One molecular proportion of silicotetraphenylamide in benzene solution interacts quite regularly with about six atomic proportions of bromine, also dissolved in benzene, provided the temperature is kept down and the addition of the halogen made very slowly. The colour of bromine disappears, and a precipitate forms from the outset consisting of aniline and bromoaniline hydrobromides. It was found, however, that three successive stages can be recognised in this interaction, and each one has been closely examined.

1. In the first stage, bromine (2 atoms) effects the removal of one of the aniline residues in the form of hydrobromide, which separates out, and there remains in solution the substituted guanidine,—



2. At the second stage, the guanidine is attacked by a similar proportion of bromine, which causes the removal of more hydrobromide and the formation of a soluble disubstituted di-imide, $\text{Si}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Br}$. This substance does not appear to form another additive compound analogous to that afforded by the unsubstituted di-imide.

3. The third stage in which another molecule of bromine acts on the substituted di-imide, is to some extent conditioned by the dilution of the benzene solution in which the interaction takes place; but the chief change involves the removal of a third aniline residue, leaving in solution the SiN compound $\text{SiN}\cdot\text{C}_6\text{H}_5\text{Br}_2$.

Under varying conditions, more or less of at least one other substance is formed, with the elimination of HBr, namely, $\text{Si}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Br}$ and, probably, a still smaller proportion of $\text{Si}=\text{N}\cdot\text{C}_6\text{H}_5\text{Br}_2$.

The nitrile, when purified as far as is at present possible, is a dark coloured, vitreous solid, fusible at about 60° . It is easily decomposed by water and alcohol, but is dissolved as a whole by pure ether, provided the temperature is not allowed to rise above 5° . At the ordinary temperature, the solution decomposes, and ethyl silicates are formed, whilst a brown precipitate slowly separates, chiefly consisting of a bromoaniline derivative.

Treatment with excess of bromine leads to the production of silicon bromide and hydrogen bromide, whilst highly brominated anilines separate.

*191. "Application of the Microscopic Method of Molecular Weight Determination to Solvents of High Boiling-point." By GEORGE BARGER and ARTHUR JAMES EWINS.

The method by which the vapour pressures of two solutions are compared by measuring microscopically the change in thickness which drops of these solutions undergo when placed in a capillary tube, was originally worked out by one of the authors for use at the laboratory temperature (*Trans.*, 1904, lxxxv., 286). A hot stage is now described, which can readily be made, and by means of which the tubes can be kept under observation at a constant temperature (up to 95°). The capillaries are fastened to a microscope slide, which is fixed with a spring inside a glass tube, about 25 m.m. wide, through which a stream of hot water flows, thus keeping the temperature constant to within one or two degrees. This tube is provided with a thermometer, and rests in a block of wood on the microscope stage.

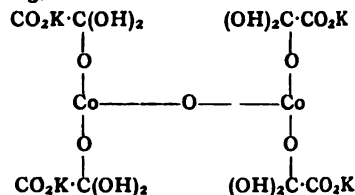
With volatile solvents, such as alcohol and benzene, 1 per cent differences in the molecular concentration of two solutions can be detected in five to ten minutes at a temperature of about 80° . With aniline, the least volatile solvent which can be conveniently employed, the corresponding time at 95° is one hour.

The solvent need not be pure; oil of turpentine, for example, gave satisfactory results. The time required for a complete determination is about an hour and a-half; for the mere verification of a probable formula, much less time is necessary. The average error in thirty determinations quoted is 3 per cent. Pyridine, acetic acid, and aniline are the best of the less volatile solvents examined.

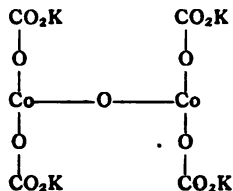
*192. "Green Compounds of Cobalt produced by Oxidising Agents." By REGINALD GRAHAM DURRANT.

Methods of obtaining green compounds by oxidising cobaltous salts in presence of the alkali salts of acetic, tartaric, citric, oxalic, lactic, malic, succinic, and glycolic acids were given. The preparation, analysis, and properties of green crystalline potassium cobaltic oxalate were set forth in detail, and evidence was adduced in support of the existence of analogous crystalline ammonium cobaltic and calcium cobaltic oxalates.

The conclusions arrived at are that (1) these substances most probably all contain the nucleus $\text{Co}\cdot\text{O}\cdot\text{Co}$, the oxalate being,—



and the carbonate—



2. The prevailing green colour in these cobaltic compounds with carboxylic salts depends on the persistence of the complex $\text{Co}\cdot\text{O}\cdot\text{Co}$.

3. The differences observable in the tints and in the absorption spectra of the various green solutions depend probably on the varied association of carboxyl groups attached to this nucleus.

*193. "Dunstan, Jowett, and Gouling's Paper on the Rusting of Iron." By EDWARD DIVERS.

The fact which throws into the background all others contained in the important paper by Dunstan, Jowett, and Gouling on the rusting of iron (*Trans.*, 1905, lxxvii., 1548), and, indeed, constitutes its substance, is that even the purest available iron is freely rusted by oxygen and

liquid water, unaided by carbon dioxide or any other substance. Yet, in the construction of the paper, this fact seems to have been subordinated, perhaps without intention, to the setting forth of, and submitting evidence for, the theory that the rusting of iron is a process involving the formation of hydrogen peroxide. Accordingly, the publication (*Proc.*, 1903, xix., 150) of a preliminary abstract of the contents of the full paper led Moody (*loc. cit.*, p. 157) to suppose Dunstan's contention to be that ordinary rusting is caused by hydrogen peroxide. There is, therefore, reason to fear that those chemists who may hesitate to accept the hydrogen peroxide theory will be apt to overlook the fact that whether with or without the intervention of hydrogen peroxide, iron rusts when in contact with nothing more than an aqueous solution of oxygen.

Now the truth of the authors' theory to explain the fact may well be doubted, although they themselves hold that they have obtained a considerable body of experimental evidence in favour of the temporary formation of hydrogen peroxide. For, in support of the theory, no other fact is to be found in the paper than that the alkalis and other substances, which interfere with the existence of hydrogen peroxide, likewise prevent the rusting of iron. But the coincidence here observed is fully and accurately accounted for, without dependence on hydrogen peroxide, as being the result of the inability of oxygen and water in presence of one of these substances to act together as *hydroxyl*, whether it be to form hydrogen peroxide, $(HO)_2$, or such a compound as zinc hydroxide, $Zn(OH)_2$. Hydrogen peroxide is not wanted in order to explain the rusting of iron; indeed, its production stands rather in the way of a simple theory. What is wanted is the presentation of free or at least available hydroxyl groups to unite with the iron. Again, it is hardly a tenable argument that a substance, because it interferes with the existence of another substance, must likewise prevent its formation. For instance, ferrous sulphate ends the existence of free chlorine, but it does not prevent manganese dioxide and hydrochloric acid in contact with it producing the atomic chlorine, which it immediately proceeds to consume.

Moritz Traube explained and experimentally illustrated what he called the "autoxidation" of metals and other substances as being the chemical intervention of the water molecule between that of the autoxidising substance and that of the oxygen. Water, which cannot be acted on by either alone, is capable of chemical partition between the two; with zinc present to seize the hydroxyl of the water, the oxygen can take the rest of its hydrogen to form hydrogen peroxide, and, accordingly, this substance is not an uncommon product of autoxidation. It is easy and natural to admit that, with the great evolution of energy in the union of zinc with hydroxyl, only the small addition of energy afforded by the hydrogenation of free oxygen into hydrogen peroxide should be sufficient to half dehydrogenate the oxygen of water. Traube's equation satisfactorily represents therefore the formation of the hydrogen peroxide. The authors, however, give equations which are indistinguishable from those suggested by Hoppe-Seyler, although they very rightly reject this physiological chemist's conception of the nature of oxidation. They write (*loc. cit.*, p. 1549) $Fe + O_2 + H_2O = FeO + H_2O_2$ [Traube would have written it $Fe + 2OH \cdot H + O_2 = Fe(OH)_2 + H_2O_2$]. Again, on p. 1564, they write $Fe + OH_2 = FeO + H_2$; $H_2 + O_2 = H_2O_2$, equations which have none of the acceptability of Traube's. Can it be admitted that iron may do what potassium cannot do, displace all the hydrogen of water? Can it be allowed by the laws of thermal chemistry that cold water can be endothermically oxidised into hydrogen peroxide? There is another equation, given to explain the action of hydrogen peroxide on iron, to which also exception must be taken: $Fe + H_2O_2 = FeO + H_2O$. Surely if the equation holds good at all, the right side of it should be written $Fe(OH)_2$, the hydroxyls uniting with the iron, even if, afterwards, water separates.

The conversion of iron into rust seems to be as fully explained and as simply displayed as the facts allow by the

following equation: $(O_2 + 2H \cdot HO) + 4Fe + 2O_2 = 4HO \cdot Fe \cdot O$, or, if preferred, $2(HO)_2Fe_2O_2$. If it is proper, as it apparently may be, to represent the ferrous and the ferric oxidation as distinct, then the above equation may be resolved into $(O_2 + 2H \cdot HO) + 4Fe + O_2 = 2(HO \cdot Fe'')_2O$ (ferrous oxyhydroxide) and $2(HOFe')_2O + O_2 = 4HO \cdot Fe'''O$. Putting these equations into words, rusting consists in the oxidation of iron by oxygen, with the intervention of water as hydroxyl hydride to the extent of two molecules for every three molecules of oxygen consumed. (Instead of the six molecules of water required by Traube's equation in the theoretical production of $Fe_2(OH)_6$). To account for the non-formation of hydrogen peroxide nothing need be advanced; that seems to come as a matter of course. The point to be explained is, rather, the very production of this substance during the autoxidation of zinc and other substances. Why do not all the hydroxyls combine with the zinc, instead of a very small proportion of them remaining as hydrogen peroxide? The equation $Zn + 2OH \cdot H + O_2 + Zn = 2Zn(OH)_2$, seems to express accurately what really does happen to a very great extent.

DISCUSSION.

The following communication from Prof. DUNSTAN was read by the Secretary:—"In the preceding note, Dr. Divers has expressed the fear that the important fact established in the paper by Drs. Jowett and Goulding, and myself, that iron will rust in an aqueous solution of oxygen without carbon dioxide will be overlooked. This fear is, however, not justified in view of the explicit statements contained in the paper and the prominence given to the experimental evidence.

"Dr. Divers is of opinion that the intermediate formation of hydrogen peroxide, suggested as a working hypothesis to account for the observed facts, is unnecessary, but the alternative view expressed by him as 'the presentation of available or free hydroxyl groups to unite with iron' is not intelligible, unless it amounts to what is virtually the same hypothesis, which accounts for the inhibiting effect of potassium dichromate as well as of alkalis.

"With regard to the mechanism of the change, it has not been suggested, as Dr. Divers supposes, that water is oxidised by hydrogen peroxide. On the contrary, Traube's view of the formation of hydrogen peroxide is accepted. The outline equations in the paper (*Trans.*, 1905, lxxviii., 1548) were not intended to do more than represent the general nature of the change, and may equally well be written to show that the metal takes the hydroxyl and not strictly the oxygen of the water. There is no exception to be taken to the condensed equations Dr. Divers gives in conclusion, but unless the intermediate formation of hydrogen peroxide is assumed, they do not explain the inhibiting effect of alkalis or of other salts. There is no evidence to show that alkalis interfere with the formation of simple hydroxides such as $Zn(OH)_2$.

"Dr. Divers fails to offer any satisfactory explanation of the undoubted formation of hydrogen peroxide during the 'rusting' of zinc, where the process at work must be strictly analogous to that which occurs in the case of iron.

Mr. A. C. CHAPMAN said that it was rather surprising that investigators who had studied the rusting of iron and the action of water on other metals in the presence of oxygen should have apparently devoted so little attention to the influence of traces of metallic impurities in the metals under observation. Such charges were, of course, electrolytic in nature, and it seemed to him very probable that in many cases the action would be very greatly modified if metals of a very high degree of purity could be used in the experiments. Dr. Divers had referred to the combined action of oxygen and water on metallic zinc, and he had recently had occasion to observe how very greatly this was affected by the presence of very slight traces of nickel, cobalt, or other metallic impurities in the zinc employed.

In reply, Dr. DIVERS referred Prof. Dunstan and also

Dr. Jowett to his foregoing note, in which it is explained that the inhibitory action of such a substance as potassium hydroxide or dichromate is fully accounted for as being due to its making oxygen and water unable to behave either as hydroxyl towards iron or as hydroxyl for becoming hydrogen peroxide. He thought with Mr. Chapman that even the purest zinc yet used may have been active upon air and water through electrolysis by means of some impurity.

He was aware that the authors had treated iron as being acted on by hydrogen peroxide, but all that he had wished to contend against had been their assumption that air and water owe their activity to a production of hydrogen peroxide. Dr. Moody had fully shown that hydrogen peroxide in pure water is inactive upon iron.

*194. "Researches on the Freezing-points of Binary Mixtures of Organic Substances; the Behaviour of the Dihydric Phenols towards *p*-Toluidine, *a*-Naphthylamine, and Picric Acid." By JAMES CHARLES PHILIP and SYDNEY HERBERT SMITH.

Investigation of the freezing-point curves demonstrates the existence of several new compounds of the above substances. As might have been expected, it was found that catechol and resorcinol were able in certain cases to form two compounds with a base; for example, catechol forms two compounds with *p*-toluidine containing the constituents in the molecular ratio of 1:1 and 1:2 respectively, and freezing at 50.4° and 41.5°. Since the 50 molecular per cent compound crystallises sluggishly, it is possible to realise metastable freezing-points on the adjacent branches of the curve. In this respect, the 50 per cent compound is similar to $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ in Roozeboom's curve for the hydrates of Fe_2Cl_6 . Resorcinol and *p*-toluidine were also found to combine in two proportions.

Quinol does not form compounds so readily as resorcinol and catechol, and in the case of quinol and *a*-naphthylamine only a slight indication of the formation of a compound is obtained in the form of an intermediate branch of the curve which does not reach a summit.

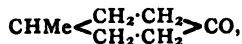
The picrates of catechol and resorcinol, as shown by the freezing-point curves, are well-defined compounds containing a molecule of each constituent. The freezing-point of catechol picrate is higher than the freezing-point of either component.

195. "Synthesis of Tertiary Menthol and of Inactive Menthene." By WILLIAM HENRY PERKIN, jun.

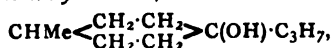
When hexahydro-*p*-toluic acid is treated with phosphorus pentachloride and bromine, it is converted into *a*-bromohexahydro-*p*-toluic acid (Perkin and Pickles, *Trans.*, 1905, lxxxvii., 645), which melts at 109–110°, and is hydrolysed by dilute sodium carbonate with formation of *a*-hydroxyhexahydro-*p*-toluic acid (m. p. 132°), and Δ^1 -tetrahydro-*p*-toluic acid. The hydroxy-acid is readily decomposed by sulphuric acid with elimination of carbon monoxide, and the solution, on dilution with water, yields 1:4-methylcyclohexanone (b. p. 170°):—



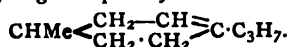
yields—



considerable quantities of Δ^1 -tetrahydro-*p*-toluic acid being produced at the same time. 1:4-Methylcyclohexanone reacts readily with magnesium isopropyl iodide, and is converted into tertiary menthol,—



which distils at 95° under 25 m.m. pressure (compare Baeyer, *Ber.*, 1893, xxvi., 2270), and when digested with potassium hydrogen sulphate yields inactive menthene,—

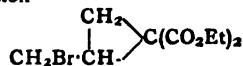


This synthetical hydrocarbon distilled at 168°, and

yielded the characteristic nitrosochloride melting at 128°; there can therefore be no doubt that it is the inactive modification of menthene (compare (Urban and Kremers, *Am. Chem. Journ.*, 1894, xvi., 395).

196. "The Synthetical Formation of Bridged Rings. Part II. Some Derivatives of Dicyclobutane." By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN.

When the sodium derivative of ethyl malonate (one molecule) is digested with tribromopropane, $\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$, an ester of the formula $\text{C}_{10}\text{H}_{15}\text{O}_4\text{Br}$ is obtained which distils at 154° (26 m.m.), and evidently has the constitution—



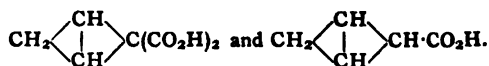
Alcoholic potash decomposes this ester with formation of a crystalline acid, $\text{C}_4\text{H}_4(\text{CO}_2\text{H})_2$, which melts at 139°, is only slowly oxidised by permanganate, and does not decolorise a solution of bromine in chloroform; it is not reduced when its solution in sodium carbonate is boiled with a large excess of sodium amalgam, and, when treated with hydrobromic acid, it is converted into *a*-hydroxy-acid, $\text{C}_4\text{H}_5(\text{OH})(\text{CO}_2\text{H})_2$, which melts at 150°.

It is readily esterified by alcohol and sulphuric acid, yielding an ester, $\text{C}_4\text{H}_4(\text{CO}_2\text{Et})_2$, which distils at 129° (22 m.m.).

When the acid $\text{C}_4\text{H}_4(\text{CO}_2\text{H})_2$ is heated, it loses carbon dioxide with formation of the corresponding monobasic acid, $\text{C}_4\text{H}_5 \cdot \text{CO}_2\text{H}$, which melts at 57°, and yields an ester, $\text{C}_4\text{H}_5 \cdot \text{CO}_2\text{Et}$, which distils at 160–161° (765 m.m.).

The monobasic acid is not reduced when its alkaline solution is boiled with excess of sodium amalgam; it does not decolorise bromine, and when treated with hydrobromic acid or hydriodic acid it yields a dihydribromide, $\text{C}_4\text{H}_7\text{Br}_2 \cdot \text{CO}_2\text{H}$ (m. p. 53°), and a dihydriodide, $\text{C}_4\text{H}_7\text{I}_2 \cdot \text{CO}_2\text{H}$ (m. p. 90°), respectively.

These and other properties seem to prove that the acids $\text{C}_4\text{H}_4(\text{CO}_2\text{H})_2$ and $\text{C}_4\text{H}_5 \cdot \text{CO}_2\text{H}$ are dicyclobutane derivatives, having respectively the formulæ—



197. "Optically Active Reduced Naphthoic Acids. Part I. Dextro- Δ^2 (or 3)-dihydro-1-naphthoic Acid." By ROBERT HOWSON PICKARD and ALLEN NEVILLE.

Dextro- Δ^2 (or 3)-dihydro-1-naphthoic acid is obtained from the *l*-menthylamine salt, which is less soluble in ethyl acetate than the corresponding salt of the laevo-acid; it has $[\text{M}]_D + 370.4^\circ$ in chloroform. The transformation of the Δ^2 (or 3)-acid into the Δ^1 -acid in the presence of sodium hydroxide proceeds as a unimolecular reaction.

198. "Hydrazino-halides Derived from Oxalic Acid." By DOUGLAS ANDERSON BOWACK and ARTHUR LAPWORTH.

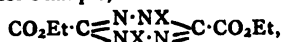
All the azo-derivatives of ethyl acetoacetate which have been examined by the authors are converted, on treatment with bromine or chlorine, into hydrazino-halides having the general formula $\text{Cl}(\text{or Br}) \cdot \text{C}(\text{CO}_2\text{C}_2\text{H}_5) \cdot \text{N} \cdot \text{NHX}$ (compare *Trans.*, 1903, lxxxiii., 1114).

(NOTE.—The term "hydrazino-" used for compounds containing the group $\text{NH} \cdot \text{N}$ = corresponds with "imino," which refers to those including the radicle $\text{N} =$).

The halogen atom in these compounds is very difficult to remove except in alkaline solution. With aqueous ammonia, the halogen is replaced by amidogen, whilst prolonged action of the agent leads to the further replacement of the ethoxyl group; the resulting compounds, $\text{NH}_2 \cdot \text{C}(\text{CO}_2 \cdot \text{C}_2\text{H}_5) \cdot \text{N} \cdot \text{NHX}$ and $\text{NH}_2 \cdot \text{C}(\text{CO} \cdot \text{NH}_2) \cdot \text{N} \cdot \text{NHX}$ are yellow, and feebly basic in character. The members of the former class may be converted into the corresponding carboxylic acids, which lose carbon dioxide when heated.

Solutions of the hydroxides or carbonates of the alkali metals act very rapidly on the hydrazino-halides, and con-

denation products which are probably dihydrotetrazine derivatives; for example,—



are obtained. These compounds form deep red crystals with a blue reflex.

199. "The Action of Nitrogen Sulphide on Organic Substances." (Part III.) By OLIVER CHARLES MINTY DAVIS.

The investigation of the action of nitrogen sulphide on the aldehydes has been continued, and it has been found that the reaction is not so general as was expected. Cinnamaldehyde, salicylaldehyde, and cuminaldehyde do not react to any extent, and the yields in other cases are very small. The nitrobenzaldehydes experimented with give the corresponding cyanidine derivatives, and an interesting example of steric hindrance is illustrated in the case of *o*-chlorobenzaldehyde, which is not appreciably decomposed, whereas the 1:4-compound readily yields the cyanidine derivative. A similar instance is noticed in the case of *o*-methoxybenzaldehyde, which furnishes a small amount of the cyanidine derivative, the 1:4-compound previously experimented with (*Trans.*, 1904, lxxxv., 1535) giving a good yield of the cyanidine, in addition to a sulphur compound and an anisamidic sulphate. Piperonaldehyde, on the other hand, in which the ortho-position with respect to the aldehyde grouping is unsubstituted, behaves in an analogous manner to anisaldehyde.

200. "The Action of Nitrogen Sulphide on Organic Substances." (Part IV.). By FRANCIS ERNEST FRANCIS.

Nitrogen sulphide acts on acetic and propionic acids at their boiling-points with the liberation of sulphur dioxide and smaller quantities of nitrogen and the formation of the corresponding amides and diamides; in both cases ammonium sulphate and free sulphur are also formed.

The action on acetic anhydride and the halogen derivatives of acetic acid is very similar. Chloro- and bromo-acetic acids give mixtures of their corresponding amides and diamides, di- and tri-chloroacetic acids only giving rise to di- and tri-chloroacetamides respectively.

That a deep-seated decomposition of the molecule takes place in these reactions is shown by the liberation of notable quantities of carbon monoxide, together with the other gases mentioned, and, further, the formation, in varying quantity, of the ammonium haloid salt corresponding with the halogen derivative employed.

201. "Tetrazoline." (Part III.). By SIEGFRIED RUHEMANN and RICHARD WILLIAM MERRIMAN.

The authors, who have undertaken this research with the view of investigating the remarkable properties of tetrazoline, and more especially of determining the constitutions of the two compounds which this base forms with methyl iodide (Ruhemann and Stapleton, *Trans.*, 1902, lxxxi., 261), have found that the colourless substance $\text{C}_3\text{H}_7\text{N}_4\text{I}$ combines with iodine to yield the blue additive product identical with the compound which is produced along with $\text{C}_3\text{H}_7\text{N}_4\text{I}$ by the action of methyl iodide on tetrazoline. It therefore has the composition $\text{C}_3\text{H}_7\text{N}_4\text{I}_3$ instead of $\text{C}_3\text{H}_9\text{N}_4\text{I}_3$, as previously stated. The resemblance of this additive product to the periodide of diazobenzene chloride led the authors to the view that $\text{C}_3\text{H}_7\text{N}_4\text{I}$ has the constitution—



and therefore $\text{C}_3\text{H}_7\text{N}_4\text{I}_3$ the analogous formula—



It would therefore follow that the action of methyl iodide on tetrazoline,—



causes an isomerisation to—

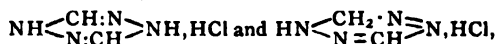


Such a transformation, as shown, takes place readily by the action of aldehydes on tetrazoline in the presence of piperidine, when compounds of the general formula—



are formed.

The authors have thus prepared a large number of condensation products, and have found that, although partially hydrolysed by hydrochloric acid, these solutions yield normal platinichlorides. The hydrolysis is complete on boiling with the dilute acid, and tetrazoline is formed together with aldehydes. The authors arrive at the conclusion that the hydrochloride of this base exists in two tautomeric forms,—



which are interchangeable. Platinic chloride is used as a means of recognising them, since the one modification forms the canary-yellow additive product, $(\text{C}_2\text{H}_4\text{N}_4)_2, \text{PtCl}_4$, previously described, whilst the other yields the orange normal platinichloride, $(\text{C}_2\text{H}_4\text{N}_4)_2, \text{H}_2\text{PtCl}_6$.

NOTICES OF BOOKS.

Handbook of Metallurgy. By Dr. CARL SCHNABEL. Translated by HENRY LOUIS, M.A., &c. Volume I. Second Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1905.

This edition of Dr. Carl Schnabel's valuable work on Metallurgy has been carefully translated from the second German edition, which was brought up to date and published in 1902. This volume contains the elements copper, lead, silver, and gold, and in the case of each metal gives its properties, physical and chemical, the occurrence and composition of all its ores, and detailed accounts of the various extraction processes, attention being called to the differences in the practice of different countries. The book is fully illustrated with diagrams and plans, and will form a valuable addition to the metallurgist's library.

The Elements of Physical Chemistry. By J. LIVINGSTON R. MORGAN, Ph.D. Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

In the preface to the third edition of this book the author acknowledges his indebtedness to Prof. Ostwald for suggestions and criticisms, and the influence of the writer of "Vorlesungen über Naturphilosophie" is clearly discernible in various parts of the book. This, however, is very far from being a drawback, and, indeed, beginners who find Prof. Ostwald's style rather difficult of comprehension, and those who are not capable of profiting by the study of his works at first-hand, should be grateful for a work on the same lines but very much simpler. The book, which has undergone careful revision, specially emphasises the applications of physical chemistry, and endeavours to bring into prominence the practical rather than the theoretical side of the subject, while a good collection of exercises and problems for solution will be specially useful for those who are working without the aid of a teacher.

Transactions of the American Electrochemical Society. Volume VII. Philadelphia: The American Electrochemical Society. 1905.

This volume contains the proceedings of the Seventh General Meeting of the Society, held at Boston, Mass.,

and Cambridge, Mass., in April, 1905. The Address, delivered by President Henry S. Carhart, dealt with modern developments of the theory of electrolysis, and gave a very unbiassed view of several important steps in the revision of electrolytic theories; the Address is here reproduced in full, together with other papers read before the society. One of these, by H. R. Carveth and B. E. Curry, on "Chromium and the Electrolysis of Chromic Acid" is an important contribution to our knowledge of the oxidation products of chromium and of the properties of the metal, while another on "Colloids," by W. R. Whitney, summarises the subject in a very able manner. The reports of the discussions which followed the reading of the papers adds greatly to the interest and value of the book, and while none of the papers can be described as epoch-making, some of them deal with subjects of considerable importance, and throw light upon some of the many unsolved problems of electrochemistry.

Die Elektrolyse Geschmolzener Salze. Erster Teil: Verbindungen und Elemente. ("The Electrolysis of Fused Salts. Part I. Compounds and Elements"). By RICHARD LORENZ. Halle-a-S.: Wilhelm Knapp. 1905.

This volume forms the first part of a monograph on the electrolysis of fused salts, and deals with the elements and compounds, especially from the point of view of their qualitative preparation, while in subsequent volumes the application of Faraday's law and the theory of conductivity and electromotive forces will be discussed. The chief aim which the author has kept before him has evidently been the attainment of the utmost degree of completeness possible; he gives short abstracts of all the important work which has been done on the electrolysis of elements and compounds, and has for this purpose carefully searched patent literature, passing over purely technico-constructive aspects, but otherwise entering into the question very fully. The author's statements, as far as we have been able to test them, appear to be accurate and concisely put, and as a dictionary of this particular branch of electrochemistry the monograph seems to possess every good feature.

Recherches sur le Temps que la Précipitation met à Apparaître dans les Solutions d'Hyposulphite. ("Researches on the Time taken for the Appearance of Precipitates in Hyposulphite Solutions"). By GASTON GAILLARD. Paris: Gauthier-Villars. 1905.

This monograph describes the author's painstaking researches on the causes which influence the time required for the precipitation of hyposulphites, which he has investigated with great attention to the most minute details. He gives accounts of the results he has obtained when various factors were arbitrarily altered, such as the time taken in adding one solution to the other, mixing various neutral salts with either solutions, and the degree of freshness of the solutions, &c., and illustrates these and other results by curves, giving also a chart to show the change of colour of the precipitates and variations in their external appearance; the suggested application of the work is ingenious, though it is impossible not to foresee great difficulties in connection with it. The chapter on the relations which may exist between the time certain precipitates take to appear and the thermic phenomena which accompany them, though short, contains some interesting matter, while the author shows admirable judgment in summarising and drawing conclusions from his work.

The London Essence Co. announce that they have taken over the business of the Midland Essence Company, of Church Street, Newton Heath, Manchester, for the sale of Essences, Essential Oils, Perfumery, and all articles which interest Mineral Water Manufacturers, Manufacturing Confectioners, Perfumers, Soap Makers, &c. The premises of the aforesaid Company will be used as a dépôt to facilitate the delivery of goods to northern customers.

CHEMICAL NOTICES FROM FOREIGN SOURCES

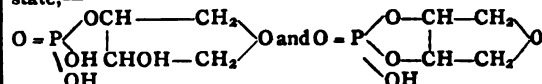
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 20, November 13, 1905.

Molecular Conductivity of Phosphoric Ethers.—P. Carré.—The author proposes to determine the molecular conductivity of some phosphoric acid ethers in order to investigate the modification that takes place in the conductivity of phosphoric acid by the partial substitution of

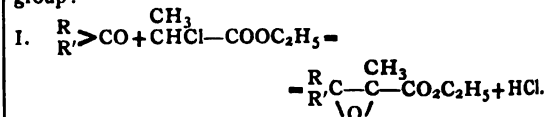
hydrogen by organic radicals, thus $O = P \begin{matrix} \text{OR} \\ \text{OH} \\ \text{OH} \end{matrix}$. He finds

that the monophosphoric ethers alone are sufficiently stable in aqueous solution for accurate determinations, which were made by Kohlrausch's method at a temperature of 25°, the inverse of the ohm being taken as the unit of conductivity. The ethers of ethyl and isobutyl alcohols, of glycol, glycerol, of erythran and mannide were prepared by the decomposition of their lead salts by means of H_2S . The author gives a table of his results, showing that for the same dilution the molecular conductivity of the ethers is appreciably higher than that of phosphoric acid, and depends on the number of carbon atoms in the radical R, and also on the function of this radical. For the same function the conductivity is less as R is greater. Thus ethylphosphoric acid has a higher conductivity than isobutylphosphoric acid, the same thing holding between glycol and glycerol derivatives, and between erythran and mannide phosphoric acids. Unfortunately for similar investigations on the di-ethers, these are not sufficiently stable in aqueous solution. But the author finds that, on determining the conductivity of a phosphoric mon-ether of a polyatomic alcohol partly transformed into a di-ether, it is higher than that of the mon-ether. Thus in erythranphosphoric acid, 35 per cent of which was in the di-ether state,—

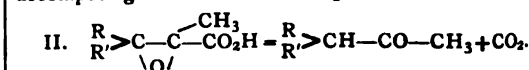


the values were 212 and 232 respectively for a dilution of 1 gm. molecule in 8. The author concludes, therefore, that the molecular conductivity of the di-ethers of phosphoric acid is probably higher than that of the mon-ethers, and that the ionisation of phosphoric ethers is considerably greater than that of phosphoric acid.

General Method for the Synthesis of the $\alpha\beta$ -Substituted Glycidic Ethers and of the Ketones.—Georges Darzens.—The author has given, in a previous note, a general method for the synthesis of β -disubstituted glycidic ethers by condensation of ketones with chloroacetic ether, and now generalises this method by substituting α -chloropropionic ether, $CH_3 \cdot CHCl \cdot CO_2C_2H_5$. By this means he gets $\alpha\beta$ -tri-substituted glycidic ethers, a hitherto unknown group:—



By saponification these give very unstable acids, easily decomposing into ketones and CO_2 :—



This, therefore, is another method for the synthesis of ketones, and the mechanism of the transformation may be explained by imagining the formation of an oxide,

$R > C - C < CH_3$
 $R \quad \quad \quad O \quad \quad H$, passing into the ketone. The author

has prepared by this method glycidic acids from several ketones, and describes them as colourless liquids with slight odour, responding to all the chemical properties to be expected from their constitution. From the acids he has prepared five new ketones, and proposes to continue his researches with more complicated ketones and other homologues of chloroacetic ether.

MISCELLANEOUS.

"Mecker" Burners and Furnaces.—Messrs. W. and J. George, Ltd., 33—37, Hatton Wall, London, E.C., are supplying these new forms of burners and furnaces. There are two models: one, using gas at ordinary pressure, produces a homogeneous flame of very high temperature, much beyond that of the usual Bunsen, and available for a variety of purposes; the second model needs feeding with air under pressure, and with it a temperature of from 1350—1400° C. can easily be reached. By some simple arrangements of fire-clay covers and supports, these burners can be converted into really powerful furnaces, capable of fusing nickel and similar metals with ease. The burners are well and strongly made and are not expensive.

Lantern Slides of Natural History Objects.—Messrs. W. Butcher and Sons, of Camera House, Farringdon Avenue, London, E.C., are issuing a series of Junior Lecturer's Lantern Slides of Natural History objects (including British butterflies, moths, birds, and reptiles). They have been produced by a colour printing process, and great pains have been taken to make them as true to nature as possible, while at the same time the price is so low that they are brought within the reach of every student. They will be found especially useful in teaching natural history in elementary schools and for home study.

On the Reduction of Oxides, and on a Method of Preparation by Aluminium of the Compound $SiMn_2$.—E. Vigoroux.—Following the work of H. Moissan on the reduction of boric anhydride by magnesium, the author investigated the decomposition of silica by magnesium and by aluminium. In 1895 he showed—(1) That the explosions obtained by Phipson, Gattermann, and others when investigating this decomposition was due to dampness; (2) that the application of a lighted match is sufficient to start the reaction throughout the whole mass; (3) that the heat generated is sufficient to melt the newly liberated silicon. In the course of his experiments the author noticed that, other things being equal, the oxide of the metal to be obtained should be chosen as high as possible, so that the heat necessary for the fusion may be greatest. For several years the author has reduced mixtures of oxides, and in this way he obtained $SiMn_2$. The reacting substances were prepared in the purest form: silica by the action of silicon chloride on water; brown oxide of manganese by the calcination of the dioxide obtained from the permanganate; aluminium was reduced to filings in the laboratory, and then freed from traces of iron by a powerful magnet. The crucible was lined with a thick layer of pure magnesia (0.5000 k.grm.) and the powdered dioxide of manganese and aluminium inserted. At the end of the reaction the contents were allowed to cool slowly. Hydrochloric and nitric acids easily attack the substance formed, and by the action of 2 per cent HCl followed by rapid washing with water acidulated with hydrofluoric acid, the author obtained crystals corresponding to the formula $SiMn_2$. This body is attacked by hot hydrochloric acid with the formation of silica. It is also affected by nitric acid, which differentiates it from that obtained by M. Lebeau.—*Comptes Rendus*, cxli., No. 19.

MEETINGS FOR THE WEEK.

- MONDAY, 11th.—Society of Arts, 8. (Cantor Lectures). "Measurement of High Frequency Currents and Electric Waves," by Dr. J. A. Fleming, F.R.S.
TUESDAY, 12th.—Society of Arts, 8. "Historical Pageants," Louis N. Parker.
— Faraday Society, 8. "Physics of Ore Flotation," by J. Swinburne and G. Rudolf. "Concentration of Metalliferous Sulphides by the Flotation Process," by A. K. Huntington. "The Ions of Pure Water," by J. Walker.
WEDNESDAY, 13th.—Society of Arts, 8. "The Commerce and Industries of Japan," by W. F. Mitchell.
THURSDAY, 14th.—Society of Arts, 4.30. "Glimpses of French Canada," by the Hon. Rodolphe Lemieux, K.C. Society of Dyers and Colourists, 8. "Method for Production of Photographs on Silk," by F. J. Farrell.
FRIDAY, 15th.—Physical, 7. (Royal College of Science, South Kensington). Exhibition of Electrical, Optical, and other Physical Apparatus.

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SCIENCE CLASSES, DAY & EVENING—

CHEMISTRY	ALEX. MCKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANE, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING	G. PATCHIN, A.R.S.M.

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Spartelite (see NATURE, March 31, 1904, page 523), 2/- per piece.
Chlorophane, 2/- per piece. Samarskite, 2/- per oz.
Zinc Sulphide, green and yellow, 5/- per tube.
Rad. Residue, 2/- per tube. Polonium, 21/- per gram; 11/- 1/4 gram.
Polonium on Bl. Rod, 25/- Willemite, 2/- per oz.
Flexible Sandstone, 5/- to 50/- (See NATURE, June 23, 1904, page 185). Radio-Active Mud, 1/6 per bottle.
Monazit, 3/- per oz. Monazit Sand, 1/- per oz.
Diamond chips and powder, 10/- per carat (best quality).
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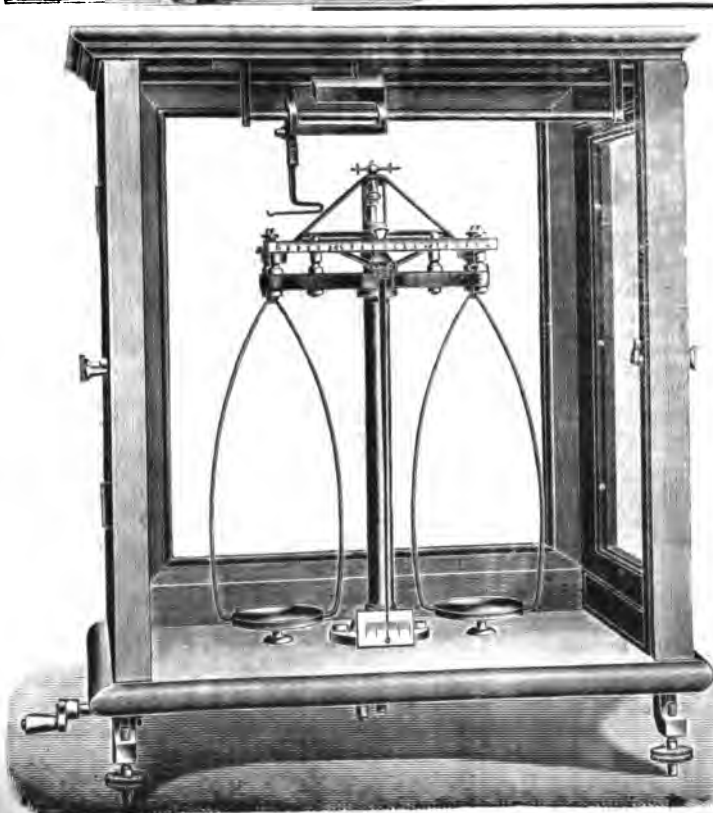
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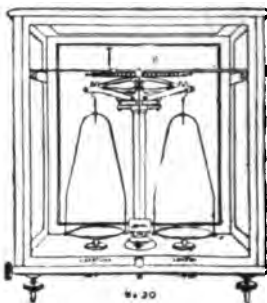
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ON SOME PHOSPHORESCENCE SPECTRA, INDICATING THE EXISTENCE OF NEW ELEMENTS.

By Sir WILLIAM CROOKES,
 Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

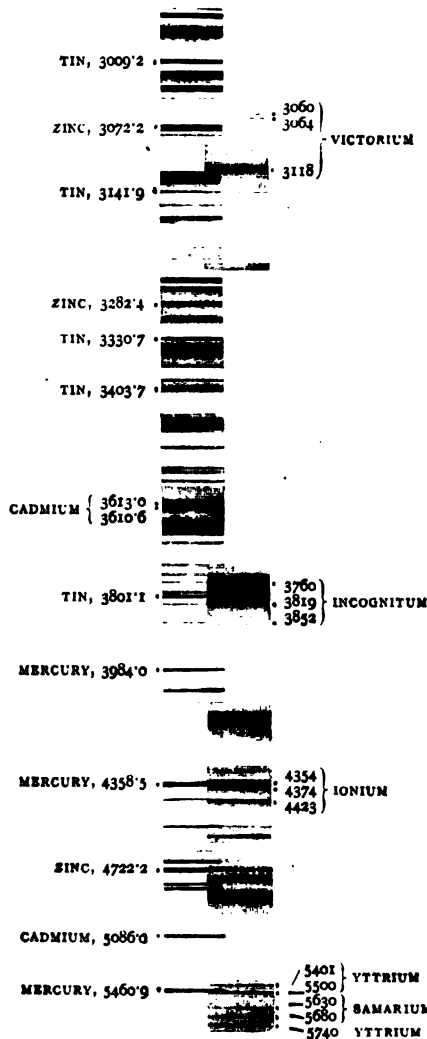
IN the course of my researches on the spectrum of the phosphorescent glow* emitted by some of the rare earths exposed to cathode rays *in vacuo*,† I have met with indications pointing to the existence of new elements. Assuming, as I think I am justified in doing from my previous work on yttrium, samarium, and victorium, that the presence of novel and special bands in a phosphorescence spectrum shown by a fractionation product of one of the yttrium or samarium group of earths may be a definite indication of a new body, I have met with at least two, and perhaps three, such groupings.

This method is an exceedingly delicate one.‡ It gives a spectrum of bands, more or less fine, easily recognised, but not so easy to measure definitely. The spectroscopist should be of low dispersion power and have a somewhat wide slit.

I can best illustrate my argument by calling attention to the accompanying drawing of the spectrum given by the phosphorescent glow of one of my fractions in which all these new groups, as well as some of those already described, are to be seen. The fine lines on the left spectrum are those of some well-known metals, photographed on the plate for the purpose of comparison, and having their wave-lengths marked; the right spectrum is that given by the earth employed. Beginning at the bottom we first see the citron line of yttrium, 5740, then come the green pair of samarium, 5680 and 5630, and closely following these are the green pair of the earth I have called G β (terbium). A gap now intervenes, in which are some faint lines and bands not identified. We now approach the limit of vision where the deep blue bands of ytterbium, 4570 and 4530, are seen. Next come three very strong lines at 4423, 4374, and 4354, which I venture to say are due to the presence of a new earth, *ionium*. A rather hazy band follows, and then appear three other bands at 3852, 3819, and 3760; these almost certainly belong to a different body to that forming the other bands, but knowing little about it, except that its partial concentration by fractionation shows it to have chemical individuality, I call it *incognitum*. After a long gap we come to the very characteristic lines of victorium, at 3118, 3064, and 3060.

Did all these separate groups show themselves equally strong in all fractions I should say they were due to the same body, but this is not the case; for taking the better known bodies, yttrium, samarium, and ytterbium, we find the special lines due to these elements wax and wane *pari*

passu with the degree of richness in which they are present in the fraction under test. One fraction which may contain excess of yttrium shows the citron line with great intensity, while the other lines of samarium or ytterbium are comparatively feeble. Another fraction, on the contrary, may show scarcely any citron line, but is rich in the double greens of samarium or the ytterbium blues. Another may have all the others faint, while the greens of G β may shine out brilliantly, and, further, a fraction may be obtained in which scarcely any bands are seen but the rich blue of ytterbium. Now, in these instances, taking the



* "Contributions to Molecular Physics in High Vacua." *Phil. Trans. Roy. Soc.*, 1879, Part II., pp. 660-1.

† "On Radiant Matter Spectroscopy: The Detection and Wide Distribution of Yttrium." *Phil. Trans. Roy. Soc.*, 1883, Part III., p. 891. "On Radiant Matter Spectroscopy; Part II.—Samarium." *Phil. Trans. Roy. Soc.*, June 18, 1885; *Phil. Trans.*, 1885, vol. clxxvi., par. 167.

‡ "On some New Elements in Gadolinite and Samarakite, Detected Spectroscopically." *Proc. Roy. Soc.*, 1886, vol. xl., p. 509.

"The radiant-matter test applied to these phosphorescing bodies proves itself every day to be more and more valuable, and one of the most far-reaching and trustworthy tools ever placed in the hands of the experimental chemist. It is an exquisitely delicate test capable of being applied to bodies which have been separated approximately, but not yet completely isolated, by chemical means: its delicacy is unsurpassed even in the region of spectrum analysis; its economy is great, inasmuch as the test involves no destruction of the specimen, and its convenience is such that any given specimen is always available for future reference. Likewise the quantity of material is limited solely by the power of the human eye to see the body under examination. Beyond all these excellences is its trustworthiness. . . . During the years in which the test has been in daily use in my laboratory, I never once have been led to view its indications with suspicion. Anomalies and apparent contradictions have cropped up in plenty; but a little more experiment has always shown that the anomalies were but finger-points pointing to fresh paths of discovery, and the contradictions were due to my own erroneous interpretation of the facts before me."

phosphorescent spectrum as a guide towards the mode and extent of fractionation, it is found not very difficult to concentrate the special band-giving earth to a greater and greater degree of isolation until we succeed in obtaining either yttrium, samarium, or ytterbium in a comparatively pure state.

Arguing from the known to the unknown, I find that, as I sub-fractionate certain portions of the rare earth fractions, I obtain earths in which one or other of the unknown groups already described grows fainter or stronger independently of the others or of the groups of lines attached to known elements. By this train of reasoning, therefore, I consider I am justified provisionally, and without undue insistence on what after all is only one of many necessary tests of newness, in saying that I am in possession of good

evidence pointing to the existence of two, if not of three, new bodies waiting to be isolated by chemical methods of fractionation.

[NOTE.—Since writing the above, I see that M. Urbain (*Comptes Rendus*, cxli., p. 954, Dec. 4th, 1905), in a paper to the Académie des Sciences, contends that the substance that I have called victorium may be a compound containing gadolinium.—W. C.]

THE ATOMIC WEIGHT OF TELLURIUM.

By A. GUTBIER.

IN order to purify the raw tellurium material, using first of all Hungarian tellurium and then 95 per cent tellurium from Dr. Theodor Schuchardt, of Görlitz, the author first separated the tellurium by reduction with sulphur dioxide, and dried it at a low temperature, after washing. The tellurium thus obtained was distilled *in vacuo*, and then part of the material was converted into telluric acid, and the rest into basic tellurium nitrate, in order to obtain a compound which could easily be purified by crystallisation. The first product, telluric acid, was prepared by evaporating a solution of the finely powdered tellurium in the purest nitric acid to dryness on the water-bath; the residue was then carefully dried at 105–110°, and suspended in the purest nitric acid. The mixture was then treated when boiling with a clear dilute solution of chromic acid, and when the last trace of tellurium dioxide had disappeared the oxidation was complete. The solution was then concentrated, and the tellurium separated out; the crystals thus obtained were heated with water on the water-bath, the liquid repeatedly filtered, and allowed to crystallise; and the crystals were re-crystallised from water. The clear colourless crystals thus obtained were completely soluble in hot water, without leaving the slightest trace of a residue. They were then dried *in vacuo*, and converted into the dioxide. The dioxide thus obtained dissolved in pure warm hydrochloric acid without yielding any chlorine, nor was any chlorine given off on boiling the solution. Thus it contained no trioxide.

The other part of the distilled tellurium was converted into the basic nitrate, which was re-crystallised twice, treated with absolute alcohol, dried, and converted into tellurium dioxide, which was also found to be perfectly free from trioxide.

The purified preparations were dissolved in hydrochloric acid, and after filtration the diluted solutions were saturated with the purest sulphuretted hydrogen free from arsenic. The precipitates were treated with freshly prepared carbon disulphide, and then with lukewarm water, filtered off, dried, pulverised, and extracted in a Soxhlet's apparatus with rectified carbon disulphide for thirty-six hours. After the residue had again been washed, dried, powdered, and extracted, pure tellurium could be isolated from it by fractionally distilling fourteen times *in vacuo*. This tellurium preparation consisted of brittle metallic particles with a metallic lustre and a crystalline fracture. The pure tellurium thus obtained was converted into the basic nitrate by Köthner's method, but as concordant results could not be obtained from this compound, even with the greatest possible care, it was converted into the dioxide as follows:—

A measured quantity of the nitrate was gently heated and allowed to cool, the operation being repeated until three consecutive weighings were constant. The tellurium was then determined:—

I. *By Reduction of the Dioxide by means of Hydrogen.*—The tellurium dioxide was weighed out in a porcelain boat, mixed with silver and quartz sand, and reduced with pure hydrogen in an air-bath at 100°; then the tube was heated to 350°, and the whole process was repeated until the weight of the tellurium was constant. In five

experiments the following atomic weights were found:—127.55, 127.60, 127.68, 127.59, 127.65.

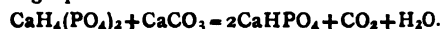
II. *By Reduction of the Dioxide by means of Hydrazine.*—The tellurium dioxide was weighed out into a platinum dish and treated at the ordinary temperature with pure dilute hydrochloric acid. Ten times the theoretical amount of freshly prepared hydrazine chlorhydrate was then added to portions of the tellurium solution in covered dishes, the mixture was gradually warmed on the water-bath, the temperature being kept at 50° for an hour, and then the water was boiled for an hour. The reduction was then complete. Three determinations gave the following values:—127.62, 127.67, 127.55.

The mean of all the eight determinations was 127.61. These results show that, however carefully tellurium is purified, the atomic weight is always found to be 127.6.—Abridged from *Lisbig's Annalen der Chemie*, vol. ccxlii., p. 266.

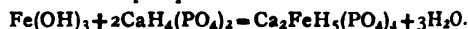
ACID VERSUS BASIC PHOSPHATIC FERTILISERS.

By W. F. SUTHERST, Ph.D., F.I.C.

PHOSPHORIC acid is applied to the soil in several forms, the principal of which are basic slag, bones, and superphosphate of lime, which, of course, are not of equal value as a plant food for the same soil, but are applied at the discretion of the farmer, who should know when and where these different sources of phosphoric acid should be spread. Superphosphate of lime being an acid salt naturally combines with all basic bodies in the soil in order to saturate or neutralise this acidity, such basic bodies being chalk, oxides of iron and aluminium, magnesia, &c. Should there be a large excess of chalk in the soil, we get a body formed, insoluble in water, but soluble in dilute organic acids—and consequently in root sap—represented by the following equation:—



But in most soils there is a large quantity of oxide of iron, generally in excess of the chalk, and under these conditions the soluble superphosphate is partly reverted to an insoluble iron and calcium phosphate:—



This double phosphate is practically insoluble in the acid root-sap, and therefore superphosphate reverted in this way is practically useless as plant food. Should there be very little of either chalk, oxide of iron, magnesia, &c., in the soil, the water-soluble phosphate is liable to be washed away from the sphere of the roots.

In the case of the bones, these are quite insoluble in pure water, but are dissolved slowly by the root-sap; as these have neither an acid nor basic reaction, their further discussion need not be undertaken.

With basic slag we get just the reverse reaction, for, being a compound of lime with phosphoric acid (the lime largely in excess), when mixed with water the mixture has an alkaline reaction. Its phosphoric acid is insoluble in water, but practically all soluble in dilute organic acids, and when mixed with the soil does not unite with any other bases, since it is fully combined already with a strong base, viz., lime. For this reason basic slag should be a more valuable manure generally than superphosphate, but its action is naturally slower, as the particles cannot come into such intimate contact with the rootlets as the distributed and reverted superphosphate. In most cases, however, an advantage can be expected by using the slag, especially on soils deficient in lime.

Some experiments on this subject were carried out on the College farm, when the effect of superphosphate, basic slag, and basic superphosphate (the latter being simply superphosphate supersaturated with lime) on the growth of mangels was tried. A piece of land was prepared, not too

rich in plant food, and on one portion superphosphate—at the rate of 400 lbs. per acre—added, in addition to 10 tons farmyard manure applied to each portion. To another basic slag was added in a sufficient quantity, so that its citric acid-soluble phosphoric acid equalled that in the superphosphate; the same with the basic superphosphate. The following yields were obtained:—

Manure.	Yield per acre.
1. Superphosphate	20 tons 12 cwt.
2. Basic slag	24 " 1 "
3. Basic superphosphate ..	24 " 19 "

The increased yield with the basic manures being about 20 and 25 per cent respectively.

The Agricultural College, Tamworth.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A GUYE.
(Continued from p. 261).

1.—The Classic Gravimetric Methods do not admit of sufficient Accuracy to Determine exactly the Second Decimal of the Atomic Weight of Nitrogen.

In order to prove this first thesis, I must first recall in a few words the principles upon which these methods rest, which are followed almost exclusively by all the scientists who are engaged upon the determination of the atomic weight of nitrogen:—

1. From the relation between ammonium chloride and silver the molecular weight of ammonium chloride is deduced, and by subtracting the atomic weights, $\text{Cl} + 4\text{H}$, the atomic weight of nitrogen is obtained; same method from the ratio $\text{NH}_4\text{Br} : \text{Ag}$.

2. By transforming a given weight of potassium chloride into nitrate, or *vice versa*, the molecular weight of KNO_3 is calculated, that of KCl being known; by subtracting the elements $\text{K} + 3\text{O}$, the atomic weight of nitrogen is obtained; the same method is applied to the ratios $\text{NaNO}_3 : \text{NaCl}$ and $\text{LiNO}_3 : \text{LiCl}$.

3. The transformation of the alkaline chlorates into nitrates, *i.e.*, the determination of the ratios $\text{KNO}_3 : \text{KClO}_3$ and $\text{NaNO}_3 : \text{NaClO}_3$ furnishes by an analogous method a new value for the atomic weight of nitrogen.

4. The transformation of silver into silver nitrate; *i.e.*, the ratio $\text{AgNO}_3 : \text{Ag}$, also the ratio $\text{AgCN} : \text{Ag}$, leads to new values for the atomic weight of nitrogen.

All these methods are indirect; they belong to the category of the methods called "of the second group"; the atomic weight found is given by an expression of the form:—

$$X = Ar - B,$$

where r is the atomic ratio determined experimentally (for example, the ratio by weight of ammonium chloride to silver for the first method mentioned above). A is a molecular weight, or an atomic weight supposed known (Ag in the example considered), and B a sum of atomic weights also supposed known ($\text{Cl} + 4\text{H}$ in the same example).

In order to judge of the accuracy of which these methods are capable, it is necessary to be exactly informed—(1) upon the accuracy realisable in the determination of the ratio r ; (2) upon the accuracy with which the quantities A and B are known.

Let us consider these points separately.

The atomic ratios r , utilised by the classic methods, are certainly among those obtained with the highest degree of agreement in this class of work, whether one examines the different determinations of a single experimenter or compares the means of the same ratio determined by different

observers. In the first case, the extremes of one series of observations are often contained between $1/8000$ and $1/15,000$; in the second case, the extremes between the means of several experimenters are generally between $1/3000$ and $1/10,000$. So as not to be too pessimistic, I will admit that these atomic ratios r are generally correct to $\pm 1/10,000$.

It is not the same for the atomic weights contained in the quantities A and B of the preceding relationship—

$$X = Ar - B.$$

These atomic weights are those of the elements Ag , Cl , Br , Li , Na , K , C . Nearly all are related more or less directly to the atomic weight of silver. It is necessary therefore to discover in the first place with what accuracy the latter is determined.

Those who have attempted to fix the most probable value of this atomic weight by utilising for the most part the same determinations, but with different combinations of the data of the experiments, have arrived at the following mean values:—

TABLE II.

	Ag for $\text{O} = 16$.
Meyer and Seubert	107.93
Ostwald	107.94
Thomsen	107.93
Clarke (1897)	107.92
Clarke (1902)	107.95
Van der Plaats	107.92

The International Table for 1905 indicates $\text{Ag} = 107.93$.

The extreme range between these different values is about $1/3000$. The accuracy with which the atomic weight of silver is known can therefore scarcely exceed $\pm 1/5000$. This is only to be expected when it is remarked that all the methods giving the atomic weight of silver depend upon that of oxygen, not directly, but always on the mean of two atomic ratios. Admitting that the error of each may be $1/10,000$ (limit of the exactitude of the gravimetric atomic ratios), and that the errors add together, the want of certainty is again expressed by the fraction $1/5000$.

This first point being admitted, it is evident that the atomic weights of the elements Cl , Br , Li , Na , K , which are only dependent upon that of silver, cannot be known with very great certainty. From the three atomic ratios it would appear logical to fix $\pm 1/3300$ as the approximate degree of accuracy to which they are determined. In fact, the correction recently made in three of Stas's atomic weights, set forth in Table III., fully justify this conclusion.

TABLE III.

Elements.	Recent values for $\text{Ag} = 107.93$.	Values calculated by Clarke (1897).
Iodine	126.970	126.847
Chlorine	35.473	35.447
Sodium	23.008	23.048

The ranges are $1/1000$ for I , $1/1360$ for Cl , and $1/576$ for Na !

Nevertheless, in order to simplify the calculation of the possible errors, we will admit that all the atomic weights to which that of nitrogen is referred are known correct to $1/5000$. If this decision is found a little too rigid for silver, it must be remembered that it is very broad for the other elements which depend on it, Cl , Br , Li , Na , K .

These fundamentals being given, it is easy to calculate the error ΔN incurred in determining the atomic weight of nitrogen by one of the methods of the second group. In this estimation two extreme cases may first be mentioned:—

(1) The errors are all of the same sign, and add together; (2) the errors are of alternate sign, so as to compensate one another as far as possible. Given that for a first approximation, the mean error attributable to this method is equal to the mean of these two extreme values both taken with the same sign, we arrive at a mean value of ΔN , to which it is interesting to fix the numerical magnitude. The following are the results obtained from this method of

* From the *Bulletin de la Société Chimique de Paris*, 1905.

calculation with the limits of accuracy above indicated, i.e., $\pm 1/10,000$ for the ratio r , and $\pm 1/5000$ for the atomic weights Ag, Cl, Br, Li, Na, K:—

TABLE IV.—*Limit of the certain Accuracy of the Atomic Weight of Nitrogen Determined by the various Classical Methods.*

Methods of the atomic ratios.	Mean ΔN .
1. $\text{NH}_4\text{Cl} : \text{Ag}$	± 0.013
2. $\text{NH}_4\text{Br} : \text{Ag}$	0.027
3. $\text{KNO}_3 : \text{KCl}$	0.020
4. $\text{NaNO}_3 : \text{NaCl}$	0.017
5. $\text{LiNO}_3 : \text{LiCl}$	0.014
6. $\text{AgNO}_3 : \text{Ag}$	0.039
7. $\text{KNO}_3 : \text{KClO}_3$	0.020
8. $\text{NaNO}_3 : \text{NaCl}$	0.017
9. $\text{AgCN} : \text{Ag}$	0.037
10. $\text{NH}_3 : \text{HCl}$	0.003

An examination of these numbers shows that not one of the classical methods (1 to 9) is susceptible, from the actual knowledge of the elements upon which they depend, of giving a value for the atomic weight of nitrogen of which the second decimal place can be guaranteed; the range of uncertainty in these methods lies between 1 and 4 units in the second decimal place; it would be greater still if a partial compensation of the errors had not been assumed, or if one took into account the real magnitude of the errors recently discovered in several atomic weights supposed known. (See Table III.).

It is not to be concluded that all the results of so much labour should be rejected wholesale, or that no method of the second group is capable of yielding accurate results. The *mean* value of ΔN from the method of Thomsen (ratio $\text{NH}_3 : \text{HCl}$), placed purposely at the end of the table, proves, on the contrary, that methods of the second group, suitably chosen, may yield perfectly accurate results.

What is certain is that classical methods are actually very ill chosen. I say "actually" because as a matter of fact there is a great disproportion between the accuracy of the atomic ratios employed and the accuracy with which the atomic weights supposed known are really so. When some day these atomic weights are determined in a more rigorous manner, the experimental results of the methods we have just discussed will very probably be utilisable afresh. The value of the atomic weight of nitrogen that is to-day deduced from them, is comparable to the topographical determination of a length by triangulation, in which the angles have been measured with a much greater accuracy than the base; when the base is known with a greater accuracy, the angular measurements will regain their full importance.

I believe in this way to have proved my first thesis:—

The classical gravimetric methods do not admit of sufficient accuracy for determining exactly the second decimal in the atomic weight of nitrogen.

Thus we are obliged, for the moment, to make an estimate of the most probable value of this atomic weight, whilst we are endeavouring to determine with certainty whether this value is 14.01 or 14.04.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Lieut. E. P. C. Amphlett, F. Bailey, H. Behrens, J. Kennedy, J. N. Kerr, and Dr. E. M. Modi were elected Members. The Special Thanks of the Members were returned to Dr. Ludwig Mond, Ph.D., D.Sc., F.R.S., for his Donation of £500 to the Fund for the Promotion of Experimental Research at Low Temperatures. It was announced from the Chair that the Managers had elected Professor William Stirling, M.D., LL.D., D.Sc., Fullerian Professor of Physiology.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

(Concluded from p. 263).

Effect of Oxalic Acid.

ONE c.c. of E.

1 c.c. of D, or 1 grm. of oxalic acid in 50 c.c., required 2.6 c.c. of titanium solution C to show the characteristic pink colour, or 0.0000275 grm. of TiO_2 .

1 c.c. of reagent was adopted as the amount best suited to use, and was the amount taken in all of the following cases unless otherwise stated.

With 0.2 grm. of oxalic acid, 0.0000339 grm. of TiO_2 in 50 c.c. gave a pink colour.

With 0.5 grm. of oxalic acid, 0.0000275 grm. of TiO_2 was required to give the test for titanium.

1.0 grm. of oxalic acid required 0.0000244 grm. of TiO_2 to give the test.

In the presence of 2.0 grms. of oxalic acid, 0.0000244 grm. of TiO_2 gave a distinct pink colour in 50 c.c., while with 5.0 grms. of oxalic acid, 0.0000265 grm. of TiO_2 gave a colour.

The amount of oxalic acid seems to have little effect although the presence of the acid diminishes the delicacy of the test, but this is independent of the amount of the acid present when more than 0.1 grm. is used.

Effect of the presence of Hydrochloric Acid.

The solution of hydrochloric acid used was one part of concentrated acid to five parts of water.

With 1 c.c. of hydrochloric acid (1 : 5) and 1 c.c. of chromotropic acid in 50 c.c., 0.0000795 grm. of TiO_2 gave a distinct pink colour.

With 2 c.c. of hydrochloric acid (1 : 5), 0.00017 grm. of TiO_2 was required to give the colour.

When 5 c.c. of hydrochloric acid (1 : 5) was used, 0.000424 grm. of TiO_2 gave a pink colour to 50 c.c.

Ten c.c. of hydrochloric acid (1 : 5) required 0.000848 grm. of TiO_2 for the colour.

Twenty c.c. of hydrochloric acid (1 : 5) required 0.00169 grm. of TiO_2 in 50 c.c. to give a definite test for titanium.

It may therefore be concluded that the destruction of the colour given by chromotropic acid is in proportion to the amount of acid present, so if this test is used hydrochloric acid should be absent.

Effect of Sulphuric Acid.

With 1 c.c. of sulphuric acid (specific gravity 1.435) 0.000318 grm. of TiO_2 was required to give a pink colour in 50 c.c. of solution.

With 2 c.c. of sulphuric acid 0.000742 grm. of TiO_2 was required to give the titanium test.

While more dilute solutions of sulphuric acid were not tried, it is evident that the effect of the sulphuric acid is roughly proportional to the amount of acid present, and that any appreciable amount of this acid seriously interferes with the delicacy of the test. The same is true of hydrofluoric acid.

In the presence of oxalic acid in any appreciable amount chromotropic acid will show 0.000025 grm. of TiO_2 in 50 c.c. very distinctly. Half that amount could be detected, but the colour is very faint, and its similarity to the colour possessed by the solution of chromotropic acid itself renders the detection of this amount uncertain. In making the test it is best to avoid the presence of free mineral acids, as they interfere, and generally in direct proportion to the amount of acid present. The neutral chlorides and sulphates are without effect, as Geisow has stated. It is probable that the colour developed in oxalate solution could be used to determine the amount of titanium present by comparison with the colour developed by known amounts of titanic acid, but this method would offer no especial advantage over the hydrogen peroxide method.

* *Proceedings of the American Philosophical Society*, 1905, xlv., p. 177.

The Action of Carbon Tetrachloride on the Oxides of Titanium, Columbium, and Tantalum.

According to Demarcay (*Comptes Rendus*, civ., 111) carbon tetrachloride vapour passed over the ignited oxides of columbium, titanium, and tantalum changes them to chlorides—in the case of titanium with the formation of an intermediate oxychloride.

Lothar Meyer (*Ber.*, xx., 681) found no action on oxide of titanium. He did not try the other two.

Delafontaine and Linebarger (*Journ. Am. Chem. Soc.*, xviii., 532) found that oxide of columbium was changed to oxychloride, CbOCl_2 , with the formation of a small amount of the chloride. In the case of tantalum the oxide was not driven from the boat, but remained behind as a pasty mass, suffering no change to chloride. They suggest this as a possible separation of the two elements columbium and tantalum.

The vapour of carbon tetrachloride was found to act slowly on ignited titanic oxide at a low red heat, some chloride of titanium being continuously formed. In time all of the oxide was converted into chloride.

The oxide of columbium is readily acted upon by carbon tetrachloride even at a low red heat. The principal product is the white oxychloride. Some of the yellow chloride is simultaneously produced. It continues to be formed in small amounts as the oxychloride is sublimed in the vapours of carbon tetrachloride. Columbium oxide heated in a sealed tube with carbon tetrachloride is completely changed to chloride after several hours at 200–225°. The chloride dissolves in carbon tetrachloride, and separates from it in large, well-formed, needle-like crystals.

The action of the vapours of carbon tetrachloride on ignited oxide of tantalum is rapid, contrary to Delafontaine and Linebarger, converting it into chloride, which can be readily freed from the carbon tetrachloride, and thus obtained pure. If the carbon tetrachloride used contains traces of moisture, oxide will be produced by the decomposition of the chloride. This oxide dissolves in the fused chloride, and remains as a glassy mass upon sublimation of the chloride. Therefore, care should be taken in the dehydration of the tetrachloride used; otherwise the product will be contaminated with oxide. This seems to be the best method for the preparation of tantalum chloride in large quantities and in a high state of purity. The chloride is an excellent starting-out material for a re-determination of the atomic weight of tantalum, a number none too definite, as a study of the series of results obtained by Marignac (*Zeit. Anal. Chem.*, v., 478) by the analysis of potassium-tantalum fluoride and ammonium-tantalum fluoride will show.

The action of carbon tetrachloride on the oxide of columbium also affords an excellent method for the preparation of the oxychloride of that element. It is produced, however, in a very voluminous state, and mats together to a tough felt, completely stopping up any tube used in its preparation. When heated in a sealed tube it condenses on a warm surface to very compact lustrous silky needles. It is very difficult to remove the last traces of columbium pentachloride from this body. This may be done, however, by subliming it in a current of chlorine over ignited oxide, but as long as any carbon tetrachloride is present the columbium chloride will continue to be formed. To make the chloride of columbium it is necessary to have recourse to the action of sulphur monochloride on the oxide, or to act on the oxide with carbon tetrachloride in a sealed tube.

Properties of Columbium Chloride.

As already mentioned, columbium chloride is soluble in carbon tetrachloride, forming a yellow coloured solution. It is much more soluble when hot than when cold, and crystallises out on cooling in well-defined crystals. It is also soluble in sulphur monochloride, the solution saturated in the hot being red in colour, and depositing yellow crystals of the chloride on cooling. It dissolves in ether with a yellow colour. On evaporating this solution on a

water-bath a thick liquid remains, and an acid vapour is given off, but no crystals separate. Upon ignition the mass chars, then burns and leaves a residue of oxide. On passing dry ammonia gas into the ethereal solution of the chloride a heavy precipitate is formed. This is ammonium chloride and columbium nitride. On washing with water the ammonium chloride is dissolved out, leaving a white residue which reverts on ignition to oxide of columbium, and when boiled with sodium hydroxide gives off ammoniacal vapours, thus pointing to nitride of columbium, probably Cb_3N_5 .

Columbium chloride containing some sulphur monochloride was treated with benzene. The sulphur monochloride dissolved out, while the columbium chloride was decomposed, leaving an insoluble gummy mass. Chloroform dissolved the chloride readily, but the solution seemed to undergo decomposition on warming and evaporating, as the liquid became brown, and a brown powder separated. No crystalline product could be procured.

The chloride is also soluble in alcohol. In the cold there is no decomposition. On warming and concentrating the solution, acid vapours were given off, due perhaps, as H. Rose has suggested, to the formation of ethyl columbate. That there is no decomposition in dilute solution is shown by the formation of the compound $\text{CbCl}_5(\text{C}_5\text{H}_{11}\text{N})_6$, which was obtained on adding piperidine to the alcoholic solution (*Zeit. Anorg. Chem.*, xxxvi., 100). Other bases, such as aniline, pyridine, &c., gave addition products which were insoluble in the solvent.

The best solvent for columbium chloride is carbon tetrachloride. In this solution reactions should take place, as they do with other chlorides, in aqueous solution; also double chlorides, analogous to the double fluorides, should be formed by bringing together solutions of the chlorides in carbon tetrachloride.

Potassium Fluoxypercolumbate.

When potassium-columbium oxyfluoride is dissolved in 3 per cent hydrogen peroxide the solution acquires a yellow colour. When a saturated solution cools, a pasty mass of crystals separates. These are very hard to free from mother-liquor. When dry, they have only a faint yellow tint. On dissolving in water containing hydrogen peroxide the solution again becomes yellow in colour. The salt obtained in this way is potassium fluoxypercolumbate of the following composition:— $\text{K}_2\text{Cbo}_2\text{F}_5 \cdot \text{H}_2\text{O}$.

Method of Analysis.

The potassium was determined as sulphate and the columbium as oxide in the usual way; that is, by expelling the fluorine with sulphuric acid, boiling with water, filtering out the insoluble columbium hydrate, and evaporating the filtrate to dryness and weighing the potassium sulphate after ignition.

The oxygen and water were determined in another sample by weighing a portion of the substance in a tube sealed at one end, covering it with a plug of ignited asbestos, connecting with a gas burette, and igniting. The oxygen was collected and measured, the tube was reweighed, the loss being water and oxygen. The water was obtained by difference.

Analysis.—0.4004 grm. of the salt gave 0.1672 grm. of oxide and 0.2196 grm. of K_2SO_4 .

0.4432 grm. of the salt lost 0.0470 grm., which contained 17.9 c.c. of oxygen at 24° and under 742 m.m. pressure, or 0.0229 grm., the difference (0.0241 grm.) being water.

	Calculated.	Found.
K_2SO_4	54.89	54.84
Oxide	42.28	41.84
O (active)	5.05	5.16
H_2O	5.68	5.44

This salt was obtained—and the above composition ascribed to it—by Piccini (*Zeit. Anorg. Chem.*, ii., 21).

He regarded it as a derivative of percolumbic acid, and not an addition product of potassium-columbium fluoride and hydrogen peroxide, because the water was lost on heating at 100°, while the oxygen did not escape until the temperature reached 150°.

On crystallising this salt from concentrated hydrofluoric acid and hydrogen peroxide in the hope of getting a perfluoride, large plates were obtained, which were quite yellow in colour, with a green tint when dry. They did not seem to differ if little or much hydrofluoric acid was used. The crystals taken for analysis were obtained from a solution consisting of one-half hydrofluoric acid (48 per cent) and one-half hydrogen peroxide (3 per cent). They were dried between filter-paper and promptly weighed out for analysis.

Analysis.—0.7260 grm. of the salt gave 0.3274 grm. of oxide and 0.3982 grm. of potassium sulphate.

0.7482 grm. of salt lost 0.0784 grm. on ignition, i.e., 29.1 c.c. of oxygen at 24° and under 742 m.m. pressure, or 0.0374 grm., the difference (0.0410 grm.) being water.

	Calculated.	Found.
K ₂ SO ₄	54.89	54.85
Oxide	42.28	42.34
O (active)	5.05	5.00
H ₂ O	5.68	5.48

Hence it may be concluded that the salt obtained from strong hydrofluoric acid is the same as that obtained when hydrofluoric acid is not used.

It would seem impossible to obtain a derivative of percolumbic acid which does not contain oxygen.

The salt separates from solutions containing hydrofluoric acid in large well-formed plates, which may be easily measured. They are much easier to handle than when crystallised from a solution free from acid. The crystals are always greenish yellow in colour.

Piccini states that the salt obtained by him had a slight yellow tint, but that this colour was completely removed by two re-crystallisations from hydrogen peroxide. The salt obtained above was re-crystallised six times from hydrogen peroxide containing hydrofluoric acid. The crystals from the last crystallisation were fully as highly coloured as those which had not been re-crystallised. They were then re-crystallised twice from hydrogen peroxide containing no acid. The resulting salt was practically colourless, but it dissolved in water and hydrogen peroxide with a yellow colour, which was intensified by the addition of hydrofluoric acid, and on evaporating again to crystallisation the crystals were as highly coloured as any obtained previously.

The oxide from the double fluoride originally used gave a colour equivalent to 0.4 per cent TiO₂. It was supposed that this colour was due entirely to titanium, and that the yellow colour of the solution and of the crystals of potassium fluoxypercolumbate was also due to this element. To test this supposition, 100 grms. of the purest potassium-columbium oxyfluoride was crystallised twice from strong hydrofluoric acid. The crystals obtained were decomposed with concentrated sulphuric acid, and the hydrate, after extraction with water, ignited to oxide. The colour which this oxide developed in oxalic acid solution with hydrogen peroxide was equivalent to 0.24 per cent of its weight of titanic acid. It was now heated in sulphur monochloride and converted into chloride. The latter, together with the excess of monochloride, was collected in a receiver, and the sulphur monochloride distilled out in the hope that any titanium tetrachloride present would be expelled with it. The chloride remaining after removing the sulphur monochloride was converted into oxide. It contained titanic oxide equivalent to 0.16 per cent. The oxide was again heated in sulphur monochloride and treated as before. After the second treatment the titanic oxide equivalent was 0.12 per cent, and the colour now developed was different. It was greenish yellow instead of yellow inclining towards red, which is characteristic of titanium. About 5 grms. of the oxide which had passed

through this treatment were changed to double fluoride and crystallised from hydrogen peroxide and hydrofluoric acid. Its solution in hydrogen peroxide was yellow, and its colour increased in intensity on adding hydrofluoric acid. The crystals from it were canary-yellow with a tint of green, differing in no respect from those previously obtained.

About 10 grms. of this yellow salt were next dissolved in water and hydrogen peroxide. This solution was distinctly yellow in colour. It was divided into two portions. To one portion 0.5 grm. of potassium-titanium fluoride was added. The colour in this portion became considerably deeper, but the excess of colour was completely discharged upon adding hydrofluoric acid, the two solutions becoming again identical in colour.

Potassium-titanium fluoride dissolved in hydrogen peroxide to a deep yellow-coloured solution. On cooling, crystals were deposited, which were not yellow but colourless when completely free from mother-liquor. The addition of hydrofluoric acid to the coloured solution completely destroys the colour, and in the presence of hydrofluoric acid the salt formed is white, resembling potassium-titanium fluoride. When air-dried it gives off neither water nor oxygen on ignition.

The only elements which give a distinctive colour in acid solution with hydrogen peroxide and which might occur here are titanium, vanadium, and molybdenum. Of these the first has been excluded and the second also, by reason of the colour which it gives (red to rose-red). There still remains molybdenum. Its colour in an oxalic acid solution with hydrogen peroxide is identical with that observed in the case of the columbium as free from titanium as it could be obtained. Although the columbium oxide used for these tests had passed through several manipulations which should remove molybdenum, such as fusion with sodium carbonate and sulphur, changing to chloride with sulphur monochloride and distilling off the more volatile portion, it was thought best to determine how much molybdenum would be required to give a test equal to that obtained from the purest oxide of the columbium at hand. To this end weighed amounts of molybdenum were dissolved in oxalic and sulphuric acids, and the colour developed with hydrogen peroxide compared with that obtained with a standard titanium solution of hydrogen peroxide.

1. 0.2780 grm. of molybdic acid developed a colour equivalent to 0.0048 grm. TiO₂, or 0.0058 grm. of molybdic acid will give a colour equal to that given under similar conditions by 0.0001 grm. TiO₂.

2. 0.0660 grm. of molybdic acid gave a colour equal to 0.0015 grm. TiO₂, or 0.0044 grm. of molybdic acid is equal to 0.0001 grm. TiO₂.

The variation in these results is due to the difficulty in matching the different shades as to intensity of colour. The average is about right, or 0.0050 grm. of molybdic acid is equivalent to 0.0001 grm. TiO₂. Calculating on this basis, the best oxide of columbium obtained, which gave a colour equivalent to 0.12 per cent TiO₂, would contain 6 per cent of MoO₃, if the colour was due to the presence of molybdenum, which would be impossible after the treatments through which the oxide has passed. It had been crystallised twice as potassium oxyfluoride, fused with sodium carbonate and sulphur, the tantalum removed, again crystallised as the oxyfluoride of potassium and twice from hydrofluoric as potassium-columbium fluoride, then changed to chloride in sulphur monochloride, the sulphur monochloride and the more volatile portions distilled off and rejected; again changed to oxide, and this treatment with sulphur monochloride repeated. The final oxide was converted into potassium fluoxypercolumbate and crystallised once from hydrogen peroxide and hydrofluoric acid. This salt was yellow in colour, and 0.3540 grm. of oxide from it, dissolved in oxalic acid, gave with hydrogen peroxide a colour equivalent to 0.000424 grm. TiO₂, or 0.12 per cent. At the most it could not have contained more than a bare trace of oxide of molybdenum.

0.3470 grm. of the oxide from the yellow fluoxypercolumbate was dissolved in oxalic acid and chromotropic acid and diluted to 50 c.c. It gave a very slight pink colour, about equal in intensity to the colour developed in 50 c.c. by 0.000025 grm. TiO_2 in the same amount of oxalic acid on treating with chromotropic acid. This would correspond to less than 0.01 per cent of TiO_2 , and is probably not very far wrong.

From these experiments it may safely be concluded that the colour produced in hydrofluoric acid solution of columbium with hydrogen peroxide is not due to the presence of titanium. Also it is probable that columbium itself gives a distinctive colour with hydrogen peroxide, equivalent to from 0.10 per cent to 0.15 per cent of its weight of TiO_2 , yet yellow-green instead of straw-yellow, as is given by titanium in dilute solutions. Possibly there may still be present some other element. For this careful search will be made.

Preparation and Analysis of the Yellow Oxide of Columbium.

Hydrated oxide of columbium, containing 10 grms. of oxide, was prepared by decomposing the double fluoride with sulphuric acid, evaporating off the excess of acid, and extracting with boiling water. This hydrate was washed repeatedly with boiling water and air-dried. It was covered with about 20 c.c. of concentrated hydrochloric acid and brought to boiling for several minutes, until all of the lumps had thoroughly disintegrated, when it was diluted to about three times its original volume with water. All but a few particles were dissolved. This solution was filtered and an equal volume of three per cent hydrogen peroxide added. It became yellow and after a few minutes a yellow precipitate appeared. The solution was allowed to stand over night. The precipitate was then filtered out, washed with cold water, in which it was insoluble, and air-dried.

Under the above conditions about one-quarter of the oxide in solution was precipitated by the hydrogen peroxide. If the remainder of the oxide in solution were recovered and dissolved in hydrochloric acid, as before, a fresh portion of it could be precipitated on adding hydrogen peroxide. The air-dried precipitate lost oxygen and water on ignition, and regained its white colour.

As the precipitation of the columbium was only partial it was best to be certain of the identity of the portion precipitated. To this end 2.5 grms. of the yellow oxide were obtained, ignited to remove the excess of oxygen, and changed to the potassium double fluoride. This analysed as follows:—

0.6822 grm. of the salt gave 0.3026 grm. of oxide and 0.3966 grm. of K_2SO_4 .

	Calculated.	Found.
Oxide	44.52	44.36
K_2SO_4	57.81	58.14

Hence the compound obtained is a derivative of columbium.

Columbium is not precipitated from the solution remaining after the yellow precipitate has been filtered out, by an excess of ammonium hydroxide, until the hydrogen peroxide in the solution has been destroyed.

Analysis of the Yellow Precipitate.—0.1917 grm. of sample gave 0.1298 grm. of Cb_2O_5 .

0.2556 grm. of sample gave 7.8 c.c. of oxygen at 22°, and under 741 m.m. pressure, equal to 0.0101 grm.

	Percentage.	Ratio.
Cb_2O_5	67.71	1.000
O (active)	3.95	0.984
H_2O (difference) ..	28.34	6.240

100.00

This corresponds to $\text{Cb}(\text{OH})_6$, or to $\text{Cb}_2\text{O}_5 \cdot \text{H}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$.

Melikoff and Pissarjewsky (*Zeit. Anorg. Chem.*, xx., 340) obtained a percolumbic acid of the formula $\text{HCB}_4 + n\text{H}_2\text{O}$, by heating columbium hydrate with 30 per cent hydrogen peroxide on a water-bath. They also obtained it by adding sulphuric acid to a solution of sodium percolumbate, dialysing out the excess of sulphuric acid and the potassium sulphate, then evaporating the clear yellow solution to dryness on a water-bath. They describe it as a yellow amorphous powder, insoluble in water.

The colour of these higher oxides seems characteristic of columbium, and is certainly not due to the presence of titanium. The hydrate obtained by Melikoff and Pissarjewsky contained twice as much active oxygen, in proportion to the columbium, as did the hydrate obtained during this investigation.

Difference in Solubility of Double Fluorides.

It is of interest to note that the solubility of potassium-titanium fluoride is increased upon the addition of hydrogen peroxide, while that of the potassium-columbium oxyfluoride is decreased. In hydrofluoric acid this order is reversed, the columbium salt becoming more soluble and the titanium salt less soluble. This suggests alternating these solvents in the crystallisation of columbium and potassium double fluorides as one of the best means for removing titanium.

Re-crystallisation from hydrofluoric acid in the form of K_2CbF_7 will remove tin and probably also tungsten from impure potassium-columbium oxyfluoride. Two re-crystallisations from that solvent are sufficient to give an oxide, the ignition of which in a platinum crucible gave no stain on the crucible. If partially dried oxide wrapped in the filter-paper be ignited directly in a platinum crucible the presence of a stain on the crucible after removing the oxide will be a very delicate test for tin. It is likely that when tin is removed by crystallisation tungsten is also, if they are present in about equal amounts and in such cases where the total amount is very small. The procedure would remove the necessity for the tedious sodium carbonate and sulphur fusions used in this work.

Behaviour with Precipitants.

Pennington (*Journ. Am. Chem. Soc.*, xviii., 38) noted that disodium-hydrogen phosphate gave no precipitate in a solution of potassium-columbium oxyfluoride, while it completely precipitated titanium from a solution of its double fluoride. This was studied briefly in order to determine if it might not serve as a quantitative separation of columbium from titanium. It was found that when the reagent was added to a solution containing a large excess of columbium and only a little titanium, no precipitate was produced even on prolonged boiling. If the amount of titanium was increased slightly, both the titanium and the columbium were completely precipitated by the disodium-hydrogen phosphate. This reagent, therefore, does not separate the two elements.

Geisow found that an alkaline formoxime solution precipitated zirconium and titanium, but did not precipitate columbium.

Formoxime, or its polymerisation product, was prepared by bringing together solutions of the calculated quantities of formaldehyde, sodium carbonate, and hydroxylamine hydrochloride. The resulting solution gave no precipitate when added to a solution of titanium as double fluoride, zirconium as double fluoride, or to a solution of columbium double fluoride. Further, after the addition of the formoxime solution, ammonium hydroxide failed to give a precipitate with any of the solutions noted above. It did, however, give a precipitate with tantalum double fluoride, but this was only partial.

The statement of Geisow that titanium and zirconium can be separated from columbium by means of an alkaline formoxime solution was not verified. The precipitation with tantalum is only partial, and not complete as stated by him.

It was noted (*Journ. Am. Chem. Soc.*, xxvi., 1248) that potassium iodate gave a complete precipitation in a solution of potassium-titanium fluoride, and no precipitate with a solution of columbium double fluoride. Potassium iodate, free from periodate, was prepared, and it was found to give no precipitate with either columbium or titanium, except in acid solution, when both were precipitated. A solution of a periodate was not tried.

NOTICES OF BOOKS.

Chemisch-technische Untersuchungsmethoden. ("The Chemical Examination of Technical Products"). Edited by Dr. GEORG LUNGE. Vol. III. Fifth Edition. Berlin: Julius Springer. 1905.

THE third volume of the latest edition of this encyclopædia of technical chemistry deals amongst other subjects with oils, caoutchouc, sugar, starch, alcoholic beverages, organic colouring matters, &c., all the articles having been revised and brought up to date. Some of the papers are entirely new and written by new authors; for instance, oils, fats, and waxes are treated very exhaustively by Dr. J. Lewkowitsch, caoutchouc and objects made of it by Dr. Fritz Frank and Dr. Eduard Marckwald, and beer by Prof. C. J. Lintner; while other sections, such as those on mineral oils and organic colouring matters, have been considerably enlarged.

Gmelin—Kraut's Handbuch der Anorganischen Chemie. ("Gmelin and Kraut's Handbook of Inorganic Chemistry"). Seventh Edition. Vol. I., Part I. Edited by A. HILGER and C. FRIEDHEIM. Heidelberg: Carl Winter. 1905.

THE revision of this handbook of inorganic chemistry, which is probably unequalled for completeness in any other language, has been most thoroughly performed, to judge by the first part of Volume I. of the seventh edition which has just appeared. Several workers have collaborated for the purpose of collecting fresh information and critically examining the text, and they hope to complete the issue of this latest edition within three or four years, so that those who now begin to purchase the parts as they appear will not have very long to wait before they are in possession of the whole work, which will be found of unique value as a book of reference.

Traité Pratique d'Electrochimie. ("Practical Treatise on Electrochemistry"). By RICHARD LORENZ. Remodelled from the German Edition by GEORGES HOSTELET. Paris: Gauthier-Villars. 1905.

THE French edition of this work is more than a mere translation of the original, the author and translator believing that the adoption of a somewhat different method of presenting the subject might add to the value of the work from the point of view of French readers. The book is divided into three parts; the first deals with the elementary laws of electrochemistry, and the second with the theory of the electrolysis of aqueous solutions, while the third and shortest part is devoted to applied electrochemistry, electrochemical analysis, and the production of substances by electrochemical means. The treatment throughout is quite elementary, and the experimental details are clearly described, so that the beginner if he follows the instructions should find no difficulty in obtaining satisfactory results; the theory of electrochemistry is also explained fully enough to enable the student to interpret his results correctly.

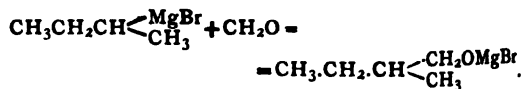
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 21, November 20, 1905.

Action of Silicon Chloride on Iron.—E. VIGOROUS.—Frémy has shown that, by this action, a silicide can be obtained crystallising in octahedral crystals, insoluble in acids and in aqua regia, having the composition Si 33 per cent, Fe 67 per cent, leading to the formula SiFe. The author has shown, by acting on other metals with the same chloride, that there is reason to consider the condition of formation of the compound SiFe₂, made known by the investigations of H. Moissan, a compound which is formed during the same reaction. As the result of three separate determinations, in which SiCl₄ was passed over reduced iron raised to just under red heat, the author obtained the silicide subliming in the delivery tube, and on analysis giving Si 20 per cent, Fe 80 per cent, leading to the formula SiFe₂. The conclusions arrived at by the author are as follows:—1. The decomposition of silicon chloride by iron takes place at a temperature below red heat. 2. The action is complete; that is to say, it takes place without the formation of the lower chlorides of silicon (since only SiCl₄ is found in the condensation apparatus). 3. The nascent silicon combines completely with the iron, leading to the formation of the alloy containing 20 per cent of silicon. 4. At this point all silication ceases under these conditions of temperature, and the reaction corresponds to the well-known formation of Fe₃Si. 5. The reaction can be represented thus:—SiCl₄ + 4Fe = Fe₃Si + 2FeCl₂. The author proposes to continue his investigations at higher temperatures, in order to ascertain the conditions of formation of the higher ferro-silicides.

Preparation of Racemic Amyl Alcohol.—P. FREUNDLER and E. DAMOND.—Racemic amyl alcohol, $\text{C}_2\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$, has up to the present only been obtained by the reduction of tiglic aldehyde and by the racemisation of the active alcohol. These two methods are not very useful, on account of the rarity of the initial compounds. The authors state that this alcohol can be prepared under much better conditions by a similar process to that of M. Locquin in the case of ordinary isoamyl alcohol, $(\text{CH}_3)_2\text{CH}.\text{CHCH}_2\text{OH}$. The method consists of condensation of the magnesium derivative of secondary butyl bromide with trioxymethylene:—



The butyl bromide was obtained by the action of phosphorus tribromide on secondary butyl alcohol obtained from the reduction of methylethylketone by the method of M. Sabatier. The retarding effect of certain substances on the formation of derivatives of magnesium has been recently shown by MM. Bischoff and Ahrens. The authors have shown this in many other cases in which this influence, far from being favourable, as for amyl alcohol, prevents completely the action of the halogen derivative on the magnesium. Especially does this happen in the preparation of triphenylcarbinol, when the commercial ether at 65° is used without acting upon it with sulphuric acid. This ether retains, indeed, aldehyde and sulphur compounds, from which it cannot be freed even by prolonged contact with sodium.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxviii., No. 14, 1905.

Action of Sulphurous Acid on the Triphenylmethane Dyes.—Karl Dürschnabel and Hugo Weil.—The authors have found that with *p*-rosaniline sulphurous acid forms compounds which possess the composition of normal salts, and they have succeeded in isolating an acid sulphite, $C_{19}H_{17}N_3O + H_2SO_3$, which is a faint pink. This compound is crystalline, and exactly resembles a rosaniline base. On treating with dilute soda solution or on boiling with water, a neutral rosaniline sulphite is obtained which, when dried at 100° , has the composition $(C_{19}H_{17}N_3)_2H_2SO_3$ (without water of crystallisation). This substance forms metallic-looking crystals, and belongs to the type of quinoid salts. Besides these two sulphites, the authors have obtained a third colourless substance, $C_{19}H_{17}N_3 \cdot H_2SO_3 + 3\frac{1}{2}H_2O$, which apparently belongs to the class of leuco-sulpho acids, described by Hantzsch and Osswald.

Decomposition of Chromic Acid by Hydrogen Peroxide.—E. H. Riesenfeld.—If a few drops of hydrogen peroxide are added to an acid chromic acid solution, the chromic acid is reduced directly to a salt of chromic oxide. No trace of a blue colouration is to be observed when this reaction occurs, the reddish yellow colour of the solution merely becoming temporarily darker, while oxygen is energetically evolved. If, however, a few drops of a chromic acid solution are added to an acid solution of hydrogen peroxide an intense blue colour appears, and afterwards changes to green, oxygen being evolved. Berthelot has already observed that the quantities of oxygen evolved in the two cases are not equal. In the first case the reaction proceeds according to the equation $2CrO_3 + 3H_2O_2 = Cr_2O_3 + 3H_2O + 3O_2$, and in the second according to the equations $Cr_2O_6 + H_2O_2 = Cr_2O_7 + H_2O$, $Cr_2O_7 + 4H_2O_2 = Cr_2O_3 + 4H_2O + 4O_2$. The end of the reaction was very difficult to determine in both cases. The experiments of Berthelot and other investigators show that the larger the excess of hydrogen peroxide used the larger is the amount of oxygen obtained. The author has found that when an excess of chromic acid is present it is decomposed by hydrogen peroxide according to the above equation in the same way as with permanganate. When chromic acid is decomposed by excess of hydrogen peroxide a perchromic acid of the formula H_3CrO_8 is formed as an intermediate product; when its salts are dissolved in acids they yield an intense blue colouration. On reducing the acid to chromic oxide salt five atoms of oxygen are set free for every atom of chromium. The amount of oxygen found experimentally is somewhat smaller than this, so that it is possible that besides the perchromic acid H_3CrO_8 an acid less rich in oxygen is formed, e.g., H_3CrO_7 . In alkaline solutions it may be assumed that the salts of the acid H_3CrO_8 are first formed. These salts are yellow or yellowish brown in dilute aqueous solution, and are decomposed in alkaline solution, yielding chromates, heat being evolved.

Boiling-points of the Alkali Metals.—Otto Ruff and Otto Johannsen.—Carnelley and Carleton Williams found that the boiling-point of potassium lies between 719° and 731° and that of sodium between 861° and 950° . Perman, employing a different method, found for sodium $743-746^\circ$ and for potassium $656-674^\circ$. The authors have now further investigated this subject, and have also determined the boiling-points of the other alkali metals, using a method of direct distillation. This could be performed (except in the case of lithium) without much difficulty, for the alkali metals do not attack iron at their boiling-points and can therefore be distilled in closed wrought iron vessels. The temperature of the vapours was determined thermoelectrically. The distilling apparatus consisted of a wrought iron tube, which widened out into a bulb at its lower end. The upper end could be closed by means of a screw-stopper through which a steel tube containing the thermo element could be passed. This retort was heated in a Röessler's gas furnace, special precautions being taken

to prevent overheating the neck of the retort. A platinum-platinrhodium thermo element was used to measure the temperature. Commercial sodium was used without any preliminary purification, but potassium was first fused under petroleum. Rubidium and caesium were prepared by heating their hydroxides with magnesium, and were then fused under petroleum. Lithium was prepared by fusing and electrolyzing a mixture of equal parts of lithium chloride and potassium chloride in a Muthmann's electrolyzing vessel, a rod of graphite being used as anode and two iron wires as cathodes. The following boiling-points were found at atmospheric pressure:—(760 m.m.): Caesium, 670° ; rubidium, 696° ($698\frac{1}{2}^\circ$); potassium, $757\frac{1}{2}^\circ$ (759°); sodium, $877\frac{1}{2}^\circ$ (879°); lithium, above 1400° . The temperatures given in brackets are the limiting temperatures which were obtained with more rapid boiling. The boiling-point of lithium could not be determined, as, contrary to previous statements, even the heat of the gas furnace was not sufficient to cause it to vapourise. At about 1400° about half the metal used remained unchanged in the retort, while the rest was converted into hydride or nitride. Even when the temperature was raised to such an extent that the wrought iron retort fused, the lithium was not vapourised, so that its boiling-point lies above 1400° . If the atomic weights of the alkali metals are taken as abscissae and their boiling-points as ordinates, a curve is obtained which rises gradually from caesium through rubidium to potassium, then somewhat more rapidly to sodium, and thence very rapidly to lithium. The curve is similar to the melting-point curve of these metals, but it does not enable the boiling-point temperatures to be expressed by a simple mathematical formula as a function of the atomic weight.

Preparation of Pure Ethyl Alcohol.—L. W. Winkler.—The following method seems specially suitable for the purification of ethyl alcohol for scientific purposes. To remove the aldehyde present silver oxide is added to the alcohol, and also some alkali hydroxide; after some days the alcohol will be found to be quite free from aldehyde, which is oxidised by the silver oxide to acetic acid, which then combines with the alkali. To remove water from alcohol metallic calcium is used. The metal in the form of turnings is allowed to act upon the alcohol in a distilling apparatus which is warmed on the water-bath. After some hours the alcohol is distilled off; it generally then contains 99.9 per cent of pure alcohol. To remove the last traces of water it is again distilled with calcium.

Electric Preparation of some New Colloidal Metals.—The Svedberg.—The author has modified Bredig's method of preparing hydrosols, using organic liquids, the metal foil being suspended in the liquid. Iron or aluminium were employed for the electrodes. Thus he very easily obtained colloidal tin, gold, silver, and lead. This method, however, is not applicable in the case of some metals; for instance, it is not possible to bring aluminium foil into solution, although the phenomena which occur are apparently exactly similar as regards the formation of sparks, &c. For these metals a second method was employed, i.e., the potential was raised and the current strength correspondingly reduced. A glass condenser of 225 sq. c.m. surface was connected in parallel in the secondary circuit of a spark inductor and the secondary pole connected with electrodes which were immersed in a porcelain dish. The metal was placed in the dish, either granulated or cut up into wire, and the liquid over it. On stopping the current a brilliant spark display occurs between the particles, the liquid becomes coloured, and in a few minutes a dark coloured solution is obtained. It is naturally an advantage to use electrodes and metallic particles of the same metal, but the influence of the electrodes is very small. By this second method colloidal magnesium was formed as an olive-green solution in absolute ethyl ether. The author has also succeeded in obtaining the alkali metals in the colloidal state. They are exceedingly unstable. Colloidal sodium is violet, and colloidal potassium blue-violet, both in ligroin, ligroin-naphthalene, and

ethyl ether. The author has also employed his method to prepare specimens of ether metals which are already known in the colloidal state.

Action of Ethane Mercarbide on Alkali Sulphides and Sulphur Chloride.—K. A. Hofmann and H. Feigl. —By the action of alcoholic alkali on mercuric oxide, $C_2Hg_6O_4H_2$ is produced; it is very stable towards acids and alkalis, but on heating to 200° or on rubbing the dried substance between paper at the ordinary temperature it explodes violently. Nitric acid, chromic acid, perchloric acid, chloric acid, and bromic acid have no action upon this substance beyond forming salts in which the molecule $C_2Hg_6O_4H_2$ functions as a base. If this base is shaken for some days with 10 per cent sulphur chloride-benzene mixture a yellow crystalline product, $C_2Hg_4Cl_2S$, is obtained; this when heated gives carbon, mercurous chloride, and a substance smelling of garlic; the constitutional formula appears to be

$$\begin{array}{c} S.S \\ | \quad | \\ (ClHg)_2C - C(HgCl)_2 \\ | \quad | \\ ClHg.CH - CH.HgCl \\ | \quad | \\ Hg.S.Hg \end{array}$$

When aqueous potassium polysulphide solution acts upon the chloride $C_2Hg_6Cl_6$ at the temperature of the room in the dark, yellow crystals of composition $C_2Hg_4Cl_2SH_2$ are obtained, the structure being

Both the mercury-carbons bonds of the hexamercuric ethane and also the other mercury bonds are very firm. The cyanide of tetramercuric ethane, $CN.Hg(Hg).C.C(Hg).Hg.CN$, is prepared by warming $C_2Hg_6O_4H_2$ with aqueous potassium cyanide solution. If aqueous potassium polysulphide solution is added to this cyanide, the CN groups and half the mercury split off, a yellow precipitate of $C_4Hg_4SH_6$ being obtained; the constitutional formula of this substance is $(Hg.CH.CH_2.Hg)_2S$. Those carbides of mercury all illustrate how firmly mercury atoms can be bound to carbon.

MISCELLANEOUS.

Catalogue of Scientific Apparatus.—We have received from Messrs. Gallenkamp and Co., Ltd., 19—21, Sun Street, Finsbury, London, E.C., a new and very fully illustrated Catalogue of General Chemical and Scientific Apparatus. Besides the description of a vast number of pieces of apparatus, the book contains some very useful tables, equivalent measures, comparison between inches, millimetres, and wire gauge, electrical measures, &c. Messrs. Gallenkamp and Co. are agents for Sartorius Balances and Weights, and some beautiful instruments of this and other makes are included. The book is carefully indexed, and seems to contain everything that can be needed in the way of apparatus for the teaching and practice of chemical and physical science.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, before Easter:—A Christmas Course of six illustrated lectures, adapted to a juvenile auditory, by Professor H. H. Turner, on "Astronomy"; Professor E. H. Parker, three lectures on "Impressions of Travel in China and the Far East"; Professor William Stirling, six lectures on Physiology subject; Dr. J. E. Marr, three lectures on "The Influence of Geology on Scenery" (The Tyndall Lectures); Rev. Canon Beeching, two lectures on "Shakespeare"; Mr. Benjamin Kidd, two lectures on "The Significance of the Future in the Theory of Evolution"; Mr. H. B. Irving, two lectures on "The English Stage in the Eighteenth Century"; Mr. Francis Darwin, three lectures on "The Physiology of Plants"; Professor B. Hopkinson, three lectures on "Internal Combustion Engines" (with Experimental Illustrations); Mr. J. E. C. Bodley, two lectures on "The Church in France"; Mr. J. W. Gordon, two lectures on "Advances in Microscopy"; Mr. M. H. Spielmann, two lectures on "George Frederick Watts as a Portrait Painter"; and Professor J. J. Thomson six

lectures on "The Corpuscular Theory of Matter." The Friday Evening Meetings will commence on January 19, when Professor J. J. Thomson will deliver a Discourse on "Some Applications of the Theory of Electric Discharge to Spectroscopy." Succeeding Discourses will probably be given by Professor S. P. Thompson. Mr. H. F. Newall, Mr. W. C. D. Whetham, Dr. R. Caton, Dr. Hutchison, Sir Andrew Noble, Bart., Professor P. Zeemann, Mr. W. B. Hardy, and other gentlemen.

University College, London.—A course of Biological Chemistry, suitable for candidates in Branch F of the Institute of Chemistry, and for B.Sc. Honours Candidates, will be held by R. H. Aders Plimmer, D.Sc., in the Physiological Department during the Second and Third Terms (January to July). The class will meet on Mondays, Wednesdays, and Fridays from 10 to 5. The subjects dealt with will include the preparation, properties, and actions of enzymes; the preparation of their principal products; the preparation and estimation of the principal carbohydrates; the preparation, crystallisation, and properties of animal and vegetable proteids, and their disintegration products. Fee for course, 10 guineas (exclusive of expense of materials). A Special Course in the methods employed for the study of Bacteria, Yeasts, and Moulds will be held, if required, in the Bacteriological Department of the College during the Second and Third Terms.

Memorandum from the White Lead Corroders' Trade Section of the London Chamber of Commerce.—*The Merchandise Marks Act, 1887.*—The White Lead Corroders' Section of the London Chamber of Commerce desire to call the attention of such of our readers who may be users of White and Red Lead, whether dealers, painters and decorators, plumbers, carpenters, and wheelwrights, &c., to the steps they have taken in the past, and are still taking to secure proper protection to the public as regards the quality of the White and Red Lead they may have necessity to use. It has come to the knowledge of the Section that users of White and Red Lead, especially small buyers, have been misled in buying as "Best," "Genuine," or other term indicating the highest quality, a lead which on analysis has been found to be adulterated, and the Section desire to draw attention to the fact that it is a distinct breach of the Merchandise Marks Act, 1887, to describe and sell as "Best," "Genuine," or other similar term, any White or Red Lead which contains any adulterant such as barytes, lime, or any other foreign added matter. The penalties attaching to the use of misleading terms under the Merchandise Marks Act are unusually heavy, and even go so far as imprisonment with hard labour, so that it behoves everyone in the trade to take due precautions against their offering or having in their possession for sale, White or Red Lead which bears a misleading description within the meaning of the Act. In this connection the White Lead Section of the Chamber are prepared to examine and report on, *free of charge*, any sample of White or Red Lead bought as "Best," "Genuine," or other term indicating of the highest quality, if a small sample of the same is sent to "The Inspector," White Lead Corroders' Trade Section, London Chamber of Commerce, Oxford Court, London, E.C. A half-pound sample will be sufficient for the purpose of analysis. It should be mentioned that the Section in their endeavours to protect the small user have undertaken several cases in different parts of the country, under the Merchandise Marks Act, against firms selling adulterated Lead as "Best" or "Genuine," and, with one exception, convictions have been obtained and heavy penalties inflicted. In this connection the Section particularly desire to urge small dealers and retail shopkeepers to take care when purchasing Genuine White and Red Lead to insist on its being marked and invoiced as such. This is necessary for their own protection, as in the event of the quality of the article sold by the retailer being challenged, he has only to produce his guarantee of quality, that is the marked keg or the invoice, and the dealer at once becomes responsible and liable to

prosecution should the article prove other than of the quality guaranteed. The Section issue this warning as they have no desire to harass the small retailer if the real offender is the firm from whom he buys. The Section will be glad to hear from such of our readers as are interested, that the action they have taken meets with their approval, and will always be pleased to answer any inquiries regarding the Merchandise Marks Act and its bearing on the White and Red Lead Trade.

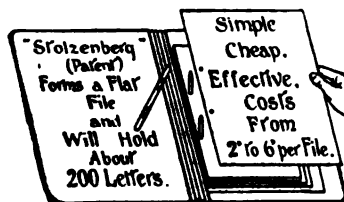
MEETINGS FOR THE WEEK.

- MONDAY, 18th.**—Society of Arts, 8. (Cantor Lectures). "Measurement of High Frequency Currents and Electric Waves," by Dr. J. A. Fleming, F.R.S.
- WEDNESDAY, 20th.**—Society of Arts, 8. "The Aërograph Method of Distributing Colour," by Charles L. Burdick. Microscopical, 8. "A 'Fern' Fructification from the Lower Coal Measures of Shore, Lancashire," by D. M. S. Watson. Exhibition of Balsam Mounted Slides by the late Andrew Pritchard.
- THURSDAY, 21st.**—Chemical, 8.30. "Relation of Position Isomerism to Optical Activity—Part V., Rotation of the Menthyl Esters of the Isomeric Dibromobenzoic Acids," by J. B. Cohen and I. H. Zortman. "Azo - derivatives from α -Naphtho - methyl - coumarin," by J. T. Hewitt and H. V. Mitchell. "Supposed Identity of Dihydrolauroleone and of Dihydro-lauroleone with 1:1-Dimethylhexahydrobenzene," by A. W. Crossley and N. Renouf. "Slow Combustion of Carbon Disulphide," by N. Smith.

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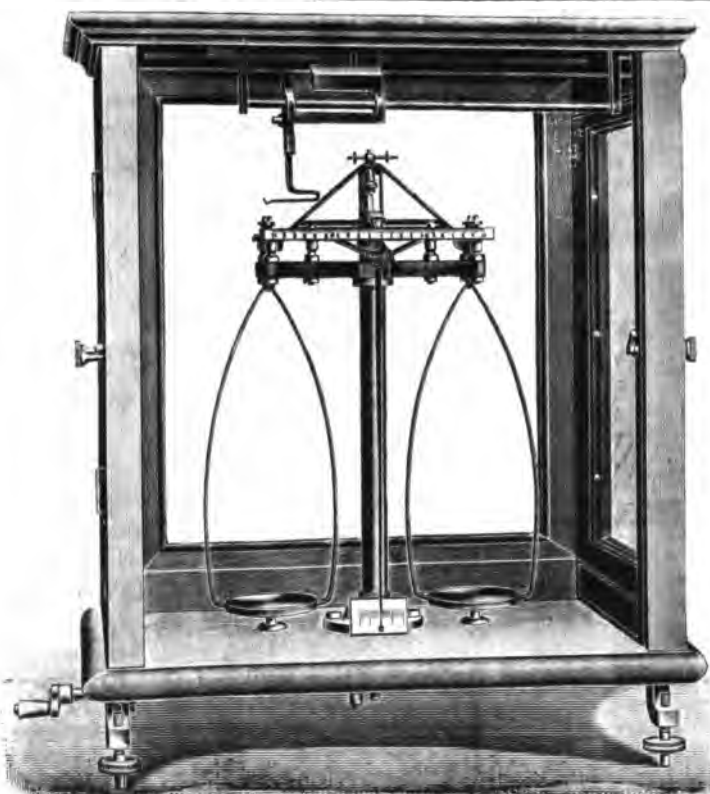
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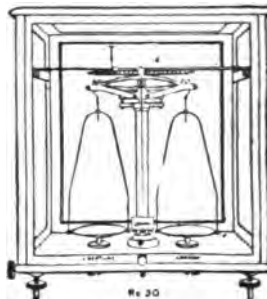
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THE CHEMICAL NEWS.

Vol. XCII., No. 2404.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A GUYE

(Continued from p. 276).

II. The Modern Physico-chemical Methods are sufficiently accurate for Determining exactly the Second Decimal of the Atomic Weight of Nitrogen.

THE importance of these methods does not appear to have been properly understood so far by all chemists. The fault is perhaps due to physico-chemists, who have not sufficiently expressed their views in order to elicit from them cause and effect. I may be permitted, therefore, to speak of the first principles, seeking to establish their co-ordination, and to place in evidence their perfect harmony; for the details the short time at my disposal obliges me to refer to original memoirs. For the sake of clearness I am forced also to leave aside the historical aspect of the question, so as to present it only in the simplest form, such as is to-day derived from memoirs of the subject.

It is a well acknowledged fact that the rule of Avogadro-Ampère is only the expression of an approximate law; gases or vapours have coefficients of expansion, nearly identical, it is true, but at the same time sufficiently different to make it impossible to merge them into a common value. From the result of applying Avogadro-Ampère's rule to the determination of the molecular weights of gases, taking one of them—oxygen, for example—as the standard, one obtains for the same gas slightly different values, according to the conditions of temperature and pressure during the operation; in certain cases the divergence from the theoretical value exceeds 2 per cent. Example, sulphurous anhydride at 0°.

In other words, in order to utilise the densities of gases for the exact and rigorous determination of their molecular weights, and, consequently, the atomic weights of the elements of which they are composed, it is necessary to subject these densities to a correction depending on the conditions of temperature and pressure of the operation.

We are now in the position to fix the value of this correction by four different methods, utilising different experimental data, and—a fact really worthy of attention—these methods of correction may all be based upon the characteristic equation of Van der Waals, the relation which has proved so fruitful in science.

Van der Waals' equation, reduced to unit volume—

$$\left(p + \frac{a}{v^2}\right)(v - b) = (1 + a)(1 - b)(1 + at) \dots (1),$$

furnishes the exact enunciation of Avogadro-Ampère's rule. From this it is deduced that at normal temperature and pressure the volumes of different gases containing exactly the same number of molecules are as the numbers—

$$\frac{1}{(1+a)(1-b)}, \frac{1}{(1+a')(1-b')}, \frac{1}{(1+a'')(1-b'')}, \&c.,$$

the constants $a, b, a', b', a'', b'', \&c.$, referring to the different gases in question.

These constants being much less than unity (for gases at 0° they are less than 0.01), the above numbers approximately.

If L represent the weight of a normal litre of gas (*i.e.*, at normal temperature and pressure, $h=0, \lambda=45^\circ$), then

will necessarily be between the molecular weight M and the weight L the relation—

$$M = \frac{RL}{(1+a)(1-b)} \dots (2);$$

R being a common constant for all the gases depending on the choice of units.

In the litre.-gram.-atm. system, and reducing the molecular weights to $O_2=32$, the most probable value of R is—

$$R = 22.412 \text{ litres.}$$

In order to fix the exact value of the molecular weight of a gas, of which the density at 0° has been determined, it is also necessary to know the numerical value of the product $(1+a)(1-b)$. Many methods lead to this result.

Method by Reduction of the Critical Elements to 0° and 1 Atmosphere.—What would first occur to one's mind would be to fix the numerical values of a and b by means of Van der Waals' equation. According to this scientist, the values of the coefficients a and b may be determined numerically, when the values of the critical constants of the gas are known, at the critical temperature T_c and critical pressure p_c .

But Van der Waals' equation is itself only an approximate formula, and experience has shown that the coefficients a and b of a gas, instead of remaining constant, vary in an appreciable manner with the temperature and pressure. It is only quite recently that these variations have been represented with a sufficient exactitude to satisfy rigorously the above relation (2). If the values of the coefficients a and b at normal temperature and pressure be represented by a_0 and b_0 , the formula giving the exact molecular weight becomes—

$$M = \frac{22.412 L}{(1+a_0)(1-b_0)} \dots (3).$$

Hence the name *method by reduction of the critical elements at 0° and 1 atmosphere* given to this process of calculation.

The calculation is most simply made by sub-dividing the gases into two groups, according as their critical temperature is inferior (permanent gases) or superior (liquefiable gases) at 0°. For *permanent gases* the relation (3) is replaced by the following:—

$$M = \frac{(22.412 + mT_c) L}{(1+a)(1-b)};$$

where $m=0.0000623$. This makes—

$$(1+a_0)(1-b_0) = (1+a)(1-b) - 0.00000210 T_c,$$

keeping to the general expression—

$$M = \frac{22.412 L}{(1+a_0)(1-b_0)}.$$

For *liquefiable gases*, relation (3) serves by calculating a_0 and b_0 from the formulæ—

$$a_0 = a \left(\frac{T_c}{T}\right)^{\frac{1}{2}}, \quad b = b \left(1 - \frac{T_c - T}{T_c}\right)(1 - \beta p_c);$$

where $\beta=0.0032229$.

In all these formulæ, a and b represent the constants of the equation reduced to unit-volume; these constants are calculated by means of the elements T_c and p_c obtained by experiment.

Without remaining longer over these details, it is interesting to note (Table V.) the results obtained with gases whose densities are the best known, making temporarily an approximation for nitrogen and gaseous compounds of nitrogen, since the atomic weight of this element is under discussion.

TABLE V.—Molecular Weights by Reduction of the Critical Elements.

O ₂ (standard) ..	32	CO ₂	44.003
H ₂	2.0153	C ₂ H	26.018
Ar	39.866	HCl	36.484
CO	28.001	SO ₂	64.065

* From the *Bulletin de la Société Chimique de Paris*, 1905.

A system of atomic weights is easily deduced from these numbers, which are thus determined by observations exclusively physico-chemical, and each by an independent method.

TABLE VI.—Atomic Weights.

Hydrogen, from H ₂	1'0077
Sulphur, from SO ₂	32'065
Carbon, from CO	12'001
" CO ₂	12'003
" C ₂ H ₂	12'002—Mean ..
Chlorine, from HCl	35'476
Argon, from Ar	39'866

The values of these same atomic weights, determined by the best acknowledged purely gravimetric methods, are—

H, 1'0076; C, 12'002; S, 32'058 to 32'074; Cl, 35'473

The agreement is certainly excellent; it will be remarked, in particular, the almost identical figures found for carbon, from the mean of the densities of the three gases CO, C₂H₂, CO₂ (Table VI.).

Method of Density-limits.—If A'₀ represent the mean coefficient of divergence from Mariotte's law between the pressure $p_1 + 1$ atm., and the pressure infinitely reduced $p_0 = 0$ atm., and V₁ and V₀ the corresponding volumes of the gases at these pressures, we obtain without difficulty, from Van der Waals' equation, the following relation:—

$$1 - A'_0 = \frac{1}{(1+a)(1-b)} \quad \dots (4).$$

For the fundamental relation above, the following might then be substituted:—

$$M = 22'312 L (1 - A'_0) \quad \dots (5).$$

the latter serving to calculate the exact molecular weights.

We have just deduced it from the equation in which it is implicitly contained; it was announced for the first time in the form of a hypothesis, which may be stated thus:—

The rule of Avogadro-Ampère is a law-limit; it is rigidly true at zero-pressure.

This hypothesis seems to us to-day to follow from Van der Waals' formula, to which it seemed to me good to refer it, for it is always wise to reduce the number of hypotheses used in science.

This mode of action presents also another advantage to which we shall have occasion to return.

The application of the relation (5) requires the knowledge of the coefficient A'₀. Berthelot has shown that in what concerns the permanent gases this coefficient might be taken as equal to that found between 1 and 2 atmospheres. For liquefiable gases, the coefficient A'₀ varies with the reduction of the pressure; the value found between 1 and 2 atmospheres cannot therefore be used directly—it must be subjected to a correction, the method of calculating which has been also pointed out by Berthelot.

It seems, however, that this correction is not yet altogether sufficient; it will certainly be improved upon finally; furthermore, the direct determination of the compressibility under pressures near zero presents experimentally three great difficulties; it may be asked whether these difficulties have been all surmounted by the beautiful researches of Ramsay and Steele on the density-limits of organic compounds in the gaseous state. In the meantime to avoid discussion I will only apply the method of density-limits to the permanent gases, and will endeavour to demonstrate the perfect agreement of these results with those of the preceding method.

If these two methods agree, we have the identity—

$$1 - A'_0 = \frac{1}{(1+a_0)(1-b_0)},$$

which, considering the minuteness of the different terms of the unit, becomes—

$$A'_0 = a_0 - b_0 = a - b - 0'00000210 T_c,$$

n the case of the permanent gases.

The data of Table VII. justify the correctness of this conclusion.

TABLE VII.

Gas	A' ₀ (Chappuis).	A' ₀ (Rayleigh).	A' ₀ (Jaquerod and Scherer).	(a ₀ -b ₀) by the critical constants.
O ₂ ..	—	0'00094	0'00097	0'00095
H ₂ ..	-0'00058	-0'00053	-0'00052	-0'00052
CO ..	—	0'00081	—	0'00084
NO ..	—	—	0'00117	0'00104
N ₂ ..	0'00043	0'00056	—	0'00074
Ar ..	—	—	—	0'00090

It follows from these figures that the correction factor $1 - A'_0$ or—

$$\frac{1}{(1+a_0)(1-b_0)},$$

calculated by the two methods, agree within a few hundred thousandths—the divergence is greatest for nitric oxide and nitrogen; even in this case the divergence is only of the ten-thousandth order.

This shows that, with the same densities as those used for Table V., the method of density-limits (Formula 5) leads to practically the same values for molecular weights, and, consequently, to the same atomic weights as those placed in Table VI.

Method of the Corresponding Vapour Densities.—This method also depends upon a theorem formulated by Van der Waals in connection with the celebrated theory of corresponding states. The illustrious physicist has proved that, between the densities d_1 and d_2 of two gases, determined under corresponding conditions of temperature T₁ and T₂, and of pressure p_1 and p_2 , there is the relation—

$$\frac{d_1}{d_2} = \frac{M_1}{M_2} \frac{p_{c1}}{p_{c2}} \frac{T_{c1}}{T_{c2}} \quad \dots (6);$$

M₁ and M₂ being the molecular weights of the two gases, T_{c1}, p_{c1}, and T_{c2}, p_{c2} their critical constants.

By reason of the conditions of correspondence this relation may be written—

$$\frac{d_1}{d_2} = \frac{M_1}{M_2} \frac{p_1}{p_2} \frac{T_2}{T_1}, \text{ or } \frac{d_1 T_1}{p_1} : \frac{d_2 T_2}{p_2} = \frac{M_1}{M_2} \quad \dots (7).$$

At a nearly constant factor $d_1 T_1 / p_1$ and $d_2 T_2 / p_2$ represent the vapour densities determined at T₁ and p₁ for the first gas, and at T₂ and p₂ for the second gas, then reduced to 0° and 1 atmosphere by the formulae of perfect gases (Mariotte and Gay-Lussac's laws). Thence the fundamental theorem:—

The densities of gases, determined under corresponding conditions of temperature and pressure, reduced to 0° and 1 atmosphere by the formulae of the perfect gases, are rigidly proportional to the molecular weights of these gases.

This theorem, which has only lately been demonstrated, was formulated some years ago by Leduc, as a result of his experimental researches on gases.

Properly speaking, its direct verification constitutes the method of corresponding vapour densities.

Unfortunately the elements of verification are not numerous. For want of direct determinations under corresponding conditions, the densities at 0° and 1 atmosphere may be used, when the coefficients of expansion and compressibility of the gases considered are accurately known, in order to reduce them to corresponding conditions of temperature and pressure.

I shall later have occasion to mention some verifications of this order; for the moment I will merely mention certain particularly interesting cases. The first concerns the molecular weight of argon; its critical constants coincide almost exactly with those of oxygen.

	T _c	p _c	L.
Oxygen	154'2	50'8	1'4290
Argon	152'0	50'6	1'7802

From this it follows that, at 0° and 1 atmosphere, the two gases are in corresponding conditions, the same as at all equal temperatures and pressures; the exact molecular weight of argon may therefore be deduced from the simple ratio of the densities, which gives—

$$\text{Ar} = 32 \cdot \frac{1.7802}{1.4290} = 39.865.$$

By the method of reduction of the critical elements we found (Tables V. and VI.)—

$$\text{Ar} = 39.866.$$

The agreement leaves nothing to be desired.

A second particular case is that in which the two gases compared are considered at the temperatures at which they rigidly follow Mariotte's law and Avogadro-Ampère's law. Berthelot has shown that this temperature is equal to $2.45 T_c$; for brevity, I will give it the name of *Avogadro's temperature*. In this case the application of the theorem relative to corresponding densities reduces itself to a very simple formula when the densities at 0° are known. Let t and t' be the temperatures (centigrade) of Avogadro for the two gases, a and a' their mean coefficients of expansion between 0° and t' and between 0° and T' at a pressure of 1 atmosphere, L and L' the weights of a normal litre of the two gases, M and M' their molecular weights. We have then evidently the relation—

$$M = M' \frac{L}{L'} \frac{1 + (1 - \gamma)t'}{1 + (a - \gamma)t} = M' \frac{L}{L'} [1 + (a' - \gamma)t' - (a - \gamma)t];$$

γ is the coefficient of the perfect gases, for which may be adopted the value proposed by Berthelot:—

$$\gamma = 0.00366195 \text{ or } 0.003662.$$

A third particular case is that in which these gases are considered at very high temperatures—for example, above 1000° for gases like oxygen and nitrogen. Computation shows that the variations from the laws of Mariotte and Avogadro-Ampère represent only a few units of the hundred-thousandth order; they are therefore negligible. If the gases are not dissociated at these temperatures, the direct ratio of the densities will give without correction the ratio of the exact molecular weights. Jaquero and Perrot, experimenting with elements with reference to the determination of the melting-point of gold, found the number 14.008 for the density of nitrogen at 1067° , compared to that of oxygen taken as 16. We will return later to this result.

Method of Molecular Volumes.—The principle of corresponding densities has been verified by Leduc in the course of his remarkable researches on gases. The determination of densities at all temperatures—demanded for the direct verification of this principle—being very complicated, Leduc thought that the comparison would be more easily made by considering all gases at 0° , and by taking into account the volume occupied under these circumstances by a gm.-molecule of the gas considered. This volume, ϕ , according to the theory of corresponding states, ought to be for all gases a certain function of T/T_c and of p/p_c . The researches of Leduc on the coefficients of the compressibility and expansion of gases, led him to determine numerically the constants of the formulæ which permit the calculation of ϕ when T_c and p_c are known. The explanation of these methods of calculation being, without doubt, known to you by the detailed studies of which they have been the object, I will confine myself to pointing out the fact that the system of atomic weights adopted by this observer to satisfy the relations indicated, correspond almost exactly with those deduced from the molecular weights obtained from the reduction of the critical elements at 0° or from the density limits. I reproduce them here:—

$$H = 1.0076, C = 12.004, Cl = 35.470, S = 32.056.$$

The Accuracy attainable for the Determination of Densities.—The preceding considerations show that the

correction factors resulting from the rigid application of the law of Avogadro-Ampère may be determined in several independent ways, and that the values thus obtained agree perfectly together within the limits of experimental error.

In order to judge of the accuracy obtainable by physico-chemical methods, it is advisable to know the degree of accuracy with which the densities of the gases may be determined. As latterly the means of carrying out these manipulations have been brought to greater perfection, I will confine myself to making mention of the values found for certain gases recently investigated by different observers.

TABLE VIII.—Weights of the normal Litre of certain Gases Determined by different Observers.

Gas.	Leduc.	Rayleigh.	Morley.	Lab. Guye.
O ₂ . . .	1.4288	1.42905	1.4290	1.4292 (c)
H ₂ . . .	0.08982	[0.08998] (a)	0.089873	—
N ₂ . . .	1.2503	1.2507	—	—
CO . . .	1.2501	1.2504	—	—
CO ₂ . .	1.9763	1.9769	—	1.9768 (d)
N ₂ O . .	1.9780	1.9777	—	1.9774 (d)
SO ₂ . .	2.9266	—	—	2.9266 (c)
Ar . . .	—	1.7802	1.7801 (b)	—

(a) Lord Rayleigh has recognised that this value is too high.

(b) Ramsay.

(c) J. and P.
(d) G. and P.

Taking into account the fact that the determinations were carried out in different places, often by different methods, nearly always on gases of different origin, we realise that the agreement is very satisfactory. The extreme range of variation is 1/4800 for O₂, 1/4200 for N₂ and CO, 1/3300 for CO₂ and N₂O. Under these conditions it may be admitted, without being too sanguine, that the mean values ought to be correct to 1/5000 at least, often even to 1/10,000. The correction factors used for calculating the exact molecular weights of gases often agree to nearly 1/10,000 when the value is fixed by different methods. The degree of accuracy obtained for the three physico-chemical determinations of the atomic weight of carbon, starting with the densities of CO, C₂H₂, and CO₂, with an extreme variation of 1/6000, is a confirmation of these deductions (Table VI.).

Returning to nitrogen, the exact determination of the second decimal of its atomic weight to within one unit gives only an exactitude of 1/1400; if an accuracy of 1/5000 be granted to the physico-chemical methods, the uncertainty of the atomic weight of nitrogen will only be ± 0.003 . It may therefore be logically concluded that the modern physico-chemical methods for the determination of the molecular weights of gases and of the atomic weights of their constituents are capable of sufficient accuracy to fix the exact value of the second decimal of the atomic weight of nitrogen.

(To be continued).

The Iron and Steel Institute.—The Council of the Iron and Steel Institute have arranged that the Annual General Meeting of the Institute shall be held in London on May 10th and 11th, 1906. In place of the usual Autumn Meeting a joint meeting with the American Institute of Mining Engineers will be held in London on July 23rd to 28th. It is intended during the week following to give the American visitors an opportunity of seeing some of the iron-making districts. It is anticipated that the visiting party will include many of the leading ironmasters who entertained the Iron and Steel Institute in America in 1890 and 1904. The Lord Mayor of London has kindly consented to act as Chairman of the London Reception Committee, and to give an evening Reception at the Mansion House.

THE PHYSICS OF ORE FLOTATION.*

By J. SWINBURNE and G. RUDORF, Ph.D., B.Sc.

ARGUMENT.—Theory that bells of sulphuretted hydrogen carry up the particles of sulphide is invalid. No hydrogen sulphide evolved. Adhesion between solid and liquid. Surface tension of liquid. Their joint action. Cohesion of liquids. Sometimes enormous. Air films and adhesion. Rise of temperature reduces surface tension, which becomes zero at critical-point. Rise of temperature reduces adhesion, probably to zero at boiling-point. Raising temperature to near boiling-point thus necessary for flotation. Effect of air films. Presence of carbonates necessary.

It often happens that an invention is made by a process which is in exact accord with the original meaning of the word; that is to say, it is come upon without the inventor necessarily understanding the nature of the underlying phenomena at the time. Scientific people generally arrive on the scene at a later date with explanations which may be right, but are sometimes wrong. We therefore bring forward an explanation for criticism which we think is correct, at present at any rate.

Concentration of sulphide ores by flotation was introduced by Potter in 1901, though concentration by means of oil had been already invented by Elmore. The Elmore process, however, is not a flotation process in the same sense, and therefore does not concern us for the present. Since Potter brought forward the idea of concentration by flotation other inventors have been at work in the same direction; so we will treat the subject rather broadly.

Concentration by flotation is carried out by treating the crushed ore with a suitable solution, such as a strong solution of acid sodium sulphate, at a suitable temperature, which is near the boiling-point of water. Part of the ore then rises to the top, and is skimmed off, or otherwise separated, and this forms the concentrate.

The explanation generally given is delightfully simple. It is said that the acid liberates hydrogen sulphide from the sulphides, and the gas then sticks to the particles and carries them up. As the acid does not act on the gangue, which in such cases is largely silicious material, the gangue is not carried up; and thus the separation takes place.

This theory does not fit the facts. In the first place, the sulphides generally treated are not attacked by the acid solution, so that there is no hydrogen sulphide evolved; or, at most, it is given off in very small quantities, which are out of all proportion to the amount of material floated. The sulphides of zinc, iron, and manganese alone are attacked at all by dilute acids. It cannot therefore be the hydrogen sulphide that carries up the particles of sulphide. On the other hand, there is a considerable evolution of gas, but it is carbon dioxide, and carbon dioxide is chiefly given off by the gangue, which generally contains calcite and other carbonates, the carbonates being mostly produced by the weathering of the sulphide particles. According to the theory just given, this action, contrary to what is actually found to be the case, ought to float up either the gangue as a whole, leaving the sulphides, or it should at least float up the carbonates. The next point is that in most cases flotation does not take place at all until the temperature approaches boiling-point.

It seems probable that the whole matter is mainly a question of capillarity, or rather of adhesion and surface tension effects, and although other theories have been put forward, we think that ours, besides being very simple, explains the facts best.

Consider first the capillary attraction of the solution, or the adhesion between the solid and the liquid. This phenomenon is a little difficult to examine with surface tension also coming into play. The commonest example is the case of a barometer whose tube has been well boiled, so that there is no air or other gas in the Torricellian

vacuum, only mercury vapour. If the barometer is held slanting, so that the mercury runs right up to the top, it may then be put into its vertical position, and the mercury will remain at the top. The liquid mercury is then actually under considerable tension, and in so far as it is above the barometrical height, the mercury is supported by its adhesion to the glass, which it cannot leave. This instance is particularly to the point, because it is often supposed that mercury has no adhesion to glass, which is a mistake. It also shows that mercury has considerable adhesion to itself, or, as it is usually called, cohesion. Liquids have in this sense astonishing tensile strengths—if such a term may be used. Water will stand a pull of 5 megadynes per square centimetre, or 5 atmospheres. Berthelot filled a clean tube nearly full of water, and sealed it up with a small air bubble. He then heated the water; and under the pressure it dissolved all the air, but on cooling the air did not again separate out; the water occupied the whole space. It must therefore have been under a pull in all directions great enough to increase the volume of the water; and this force was borne by the adhesion of the liquid to the internal surface of the glass, together with its own cohesion. This shows that under certain circumstances the force of adhesion between the water and glass may be very great.

Surface tension depends on the liquid itself. It is, of course, concerned with the surface of separation of a liquid and a gas; but we may treat it, to adopt the old idea, as if the surface of the liquid were always in tension like a stretched membrane, except that the tension remains the same whether the surface be increased or diminished. It is measured in dynes per centimetre, just as the tension of the membrane might be measured by making a cut a centimetre long and stitching it up, and measuring the forces on the thread necessary to keep the lips of the cut together.

If a rod is held vertically, partly in a liquid, the adhesion will tend to make the liquid run up the sides of the rod. This movement will be opposed by gravity on the one hand and surface tension on the other. Gravity, of course, tends to keep the surface of the liquid quite level, so that it meets the rod at right angles. Surface tension, considered by itself, tends to keep the surface of the liquid as small as possible, the volume, of course, remaining constant. Thus, if the adhesion, in spite of gravity, pulls the liquid some way up the sides of the rod, the surface of the liquid is increased, and the surface tension therefore tends to prevent its rise. If there were no adhesion the surface tension would not allow the surface of the liquid to remain level where it approaches the rod, but would round the corner so as to get the least possible surface. This tendency would be upset by gravity, so that a state of equilibrium would be reached in which the surface was by no means the least for the volume; but any further reduction would be prevented by the force of gravity, which would overcome the surface tension. If the rod, as imagined, has, to begin with, no adhesion for the liquid, the liquid has a curved surface, so that the rod stands in a sort of hole in the liquid, the hole having its top belled like a trumpet. If the rod has a little adhesion the liquid will stick to it up to a level somewhat below the surface, and the liquid will then leave the surface at an angle and begin to turn over from there. As the adhesion is increased the liquid touches the rod higher and higher, and leaves the surface at a greater angle, until the surface is level, and meets the rod at right angles. If the adhesion is still greater the liquid rises against the rod, the angle changing until the liquid surface meets the surface of the rod at an acute angle in the new direction. The angle between the surface of the solid and the liquid called the contact angle thus depends on the adhesion, the surface tension, and gravity. Whether it depends at all on the gas in which the whole is immersed we do not know. The surface tension has nothing to do with the solid, while the adhesion depends both on the solid and on the liquid.

It may be well at this stage to consider briefly the question from a mathematical point of view.

* A Paper read before the Faraday Society, December 12, 1905.

Two distinct capillary forces come into play when any solid is dipped into any liquid. These are, as mentioned above, the adhesion and the cohesion.

1. *Adhesion*, the attraction between the solid and the liquid particles, is measured by the contact angle θ . If $\theta = 0^\circ$, i.e., $\cos. \theta = 1$, the liquid is said to completely wet the solid. If $\theta = 180^\circ$, i.e., $\cos. \theta = -1$, the liquid does not wet the solid at all. For values of θ between 0° and 180° , i.e., of $\cos. \theta$ between $+1$ and -1 , there is imperfect wetting.

2. *Cohesion*, the attraction between the liquid particles themselves, is measured by the surface tension T , or, according to Quincke, more correctly by T divided by the specific gravity of the liquid. "Greasy" substances are those for which the cohesion of the liquid is greater than the adhesion of the liquid to the solid. The state of perfect wetting, for which $\theta = 0$, is very difficult to obtain, and even when obtained is difficult to preserve. The angle θ gradually increases on allowing solid and liquid to stand, provided both are in contact with air or some other gas. *In vacuo* it remains more or less constant, depending on the state of perfection of the vacuum. The adhesion therefore gets less and the solid gets "greasier." For this reason it is necessary in determining surface tensions to have a continually formed clean surface, or as Greenmach expresses it, the surface must be *in statu nascendi*. In order to do this Greenmach employed Röntgen's double-funnel method.

Quincke assumed that the solid surface gets coated with a very thin film of gas. For wetted substances this film must be thinner than the sphere of action of the molecular forces (about 0.0005 m.m.) and its thickness affects the value of θ . If the thickness be more than 0.0005 m.m. the substance is getting "greasy," and the degree of "greasiness" increases with time, i.e., as the gas-film gets thicker. This idea seems to have been objected to by Voltmann, but Wüllner showed that his objections were not valid, and later Magie upheld Quincke's work, and showed that only in very special cases was $\theta = 0$. This question of the air-film will be discussed more in detail below.

We will now return to the main argument and consider the case of a particle of ore and a gas-bell. The surface tension of the liquid tends to make the surface of the liquid as small as possible consistently with its still containing the air. If the particle has no adhesion the surface of the liquid surrounding it must be considered as part of the surface which has surface tension, so that the surface will arrange itself in such a way as to be the least possible to include both the gas and the particle. If the particle is large in proportion to the gas bubble the surface will surround it, the gas filling up any inequalities and helping to allow the surface to take the spherical form. If the particle is small the result will be a gas bell with a particle nearly inside it. Imagine now the particle to be endowed with increasing adhesion. It will first attach itself to the liquid at one or more points, and the angle of contact will become more and more obtuse. As this takes place the particle gets more and more into the liquid and out of the gas-bell, until the gas-bell is sticking to one side of it. If the adhesion increases more and more the final stage is that the bell has become a sphere which just touches the particle at one point. The bell will then leave the particle. In any intermediate case, such, for instance, as a bell of gas "sticking" to the particle, the adhesion would tend to reduce the surface of the solid that is in contact with the gas, and thus to make the bell more nearly spherical. The surface tension, on the other hand, is tending to make the surface of the liquid, including that in contact with the solid, as small as possible, consistently with its containing the gas.

In order to make particles of ore float up it is therefore necessary to get adhering gas-bells, and to get these to "stick" the surface tension and adhesion must be properly related. The term "stick" is not, of course, really applicable. The particle does not stick to the air-bell. We are accustomed to think of an air-bell as if it were

something independent of the liquid, floating about in it, forgetting that its attachment to a solid is a question of capillarity and surface phenomena, but for simplicity we may talk of the bell sticking to the solid.

Most constituents of ores have too great adhesion for water or dilute acid to be easily floated. To make it possible to separate them, it is necessary either to diminish the adhesion or to increase the surface tension T of the liquid. If the particles are sufficiently small for bells to raise them, the only conditions necessary are that the bell should be formed, and that the adhesion and surface tension should be rightly proportioned. Surface tension alters with temperature. The surface tension of water at ordinary temperatures is about 75.5 dynes per centimetre, and it falls with rise of temperature, approximately according to the formula $T = T_0 - 0.152t$, until it reaches zero at the critical temperature. As far as surface tension is concerned, therefore, the higher the temperature the less chance of success. But the adhesion is a different question. The adhesion of solids and liquids has been very little studied. It varies very considerably in different substances. Those with least adherence are generally called "greasy." This is because grease has little adhesion with water. Thus such a body as stibnite, which has little adhesion, may well be described as greasy. We are so accustomed to grease as a substance with small adhesion that when we meet others we naturally think them greasy. Thus if a spoon shows little adhesion for water, you know at once that the tablemaid has not rendered it chemically clean, and the small adhesion is due to a thin film of grease. But the small adhesion of stibnite is not due to a film of organic matter. The strange thing is, however, that bodies like stibnite, which have small adhesion for water and thus resemble grease, have apparently a greater adhesion for grease, and can therefore be separated by oil according to Elmore's method. It may be, not that the stibnite and oil have great mutual adhesion, but that the surface tension of the water is the main factor in making the stibnite and oil stick together. There are in this case several factors to consider; the surface tension of the water; the surface tension of the oil; the mutual adhesion of the ore and the water; of the ore and oil, and of the water and oil; so that the question is more complicated.

(To be continued).

Electrical Preparation of Colloidal Solutions of Selenium and Sulphur.—Erich Müller and Romuald Nowakowski.—Colloidal solutions of selenium have been prepared by the reduction of neutral very dilute solutions of selenium dioxide with the calculated quantity of sulphur dioxide; also both the solid and liquid hydrosols have been obtained by adding drops of a very dilute solution of hydrazine hydrate to a warm dilute aqueous solution of selenium dioxide. The hydrosol possesses a blue fluorescence in transmitted light. To prepare the hydrosol electrically a small quantity of selenium is fused on platinum-foil, so that only a part of the foil is covered, and the cathode thus made is immersed in pure water, while a platinum-wire is used for the anode. With a low voltage solutions are obtained, which, after filtering, appear yellowish red in transmitted light in thick layers, and dirty yellow in thinner layers, while they are a whitey-red yellow colour in incident light. They are exceedingly stable, but deposit red selenium after a time. They are completely precipitated by electrolytes. Although the precipitation by electrolytes is not easy to see, its occurrence is indicated by the fact that on filtration the solutions run through colourless. Besides elementary selenium some hydrogen selenide is also formed. If a piece of platinum-foil on which some sulphur has been fused is immersed in pure water and a potential of 220 volts maintained for an hour, a milk-white solution of colloidal sulphur is formed, which smells strongly of sulphuretted hydrogen. —Ber., xxxviii., No. 15.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 7th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MR. T. W. FIRTH CLARK was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George Ernest Banner, Brooklyn, Highfield Road, Rock Ferry, Cheshire; Arthur Ernest Barker, B.A., B.Sc., 3, York Road, Chorlton-cum-Hardy; Charles Frederick Polwhele Bletchley, B.A., Downside College, Bath; Arthur Forbes Braid, Rose Mount, Dumbreck, Glasgow; William Caldwell, M.A., Mont-Cecil, Bloomfield, Belfast; Reginald William Lane Clarke, 15, Torridon Road, Hither Green, S.E.; William Boulton Conyningham, "Sandon," Ballsbridge, Co. Dublin; Frederick Watkins Evans, 3, Charlotte Street, Hull; Hans Eduard Fierz, Ph.D., Clydach-on-Tawe, Glamorg., Wales; William Henry Matthews Jones, Leyden Villa, Chester; George Frederick Wesley Martin, 14, Castle Park, Lancaster; John Edmund Pitman, B.Sc., Hartley University College, Southampton; Harold Rogerson, M.Sc., 46, Bloomsbury Street, Bedford Square, W.C.; Frank Smith, B.Sc., 407, Church Road, Smithills, Bolton; Percy Charles Thornton, 9, Cantwell Road, Plumstead, S.E.; Ronald William Tonkin, 37, Oakill Road, Putney, S.W.; Elkan Wechsler, Ph.D., 59, Petherton Road, Canonbury, N.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Adam Lawson Kelly Adam; C. Chester Ahlum; James Edward Alcock; James Albert Allison; Charles Anthony, jun.; George Henry Barbrook; Marmaduke Barrowcliff; John Coggin Browne, B.Sc.; Bryce Chudleigh Burt, B.Sc.; Joseph Edward Coates, B.Sc.; Douglas Henry Bellars Cowman; Arthur Augustine Dallman; Joseph Morgan Davey; John Llewelyn Davies, B.A.; John Doull; Harry Dunlop; John Beaconsfield Gall; Sydney Montague Haig; Alfred Hart, M.A., B.Sc.; Jack Vernon Johnson Hayman; John Michael Higgins; William Basil Hill; Isaac Berkwood Hobsbaum; Cecil Hollins; Maurice Brooks Jack; Edward Towyn Jones, B.Sc.; Herbert Drake Law, B.Sc.; Rudolph Lyon; William McCleary; Robert Drysdale MacKechnie; Harry Martin; Harry George Fletcher Micklewright, B.A.; John Dunlop Millen; Edalji Manekji Modi; Eric Haydn-Morris; John Motion; Henry Allen Dugdale Neville, B.Sc.; Francis Richard Penn; Hugh Donald Perkins; Percy Barker Phipson; Frederick John Pooler, B.Sc.; Thomas Rigby; James Frederick Fothergill Rowland, B.A.; Henry Rowley; Harold Marmion Royle; Arthur Gough Ruston, B.A., B.Sc.; Harry Nestor-Schnurmann; Douglas Temple Settrington; John Booty Tillot; Frank Tutin; George Stanley Walpole, B.Sc.; John Ledger White, D.Sc.; Gerard William Williams, B.A.

Of the following papers, those marked * were read:—

*202. "The Constitution of Nitrites. Part I. Two Varieties of Silver Nitrite." By PRAFULLA CHANDRA RAY and ATUL CHANDRA GANGULI.

It has generally been maintained that silver nitrite has a nitronic or non-oxylc constitution (Divers, *Trans.*, 1883, xliii., 455; 1885, xlvii., 205), but Emerson Reynolds seems, however, to be of opinion that "isomeric metallic nitrites of both the types (oxylc and imidic) exist which are also tautomeric in a marked degree" (*Trans.*, 1903, lxxxiii., 643).

The close analogy between mercurous nitrite and the corresponding silver compound has all along been pointed out in some of the authors' previous memoirs, and it would appear that under the action of heat the former behaves as

if it had a twofold constitution, as indicated by $\text{Hg}\cdot\text{NO}_2$ and $\text{Hg}\cdot\text{O}\cdot\text{NO}$ respectively (*Trans.*, 1903, lxxxiii., 491).

In the present communication, the authors hope to establish that silver nitrite also has this dual character, the two varieties being now described under the designation of α - and β -compounds respectively.

The α -Variety of Silver Nitrite.—This is the substance prepared by double decomposition between solutions of silver nitrate and sodium nitrite. The precipitate, consisting of a mealy crystalline powder, is drained at the pump, thoroughly washed with cold water, and dried under diminished pressure over sulphuric acid. The method of experiment was exactly the same as already described (*Trans.*, 1905, lxxxvii., 180). In the experiment of Divers and Shimidzu, after the apparatus had been exhausted the flow of mercury in the fall tube was stopped so as to allow the nitrous fumes evolved during the heating of the salt to act on the metallic silver set free, thereby favouring the formation of silver nitrate and nitric oxide (*Trans.*, 1885, xlvii., 634). In the present instance, the reverse method was followed. The rate of the flow of mercury was increased during the operation. By this arrangement the nitrous fumes were swept out of the tube almost as fast as they were generated, thus giving them much less chance of coming into contact with the silver. Moreover, these being absorbed by the caustic potash in the spiral, not only was the "soiling" of mercury in the Sprengel pump guarded against, but also the formation of nitric oxide by the secondary reaction between mercury and nitrous fumes prevented.

As it was desirable that the heating should be effected at a definite temperature, an asbestos box was made fitted up with mica windows; when the bath had reached the required temperature, the portion of the glass tube containing the substance was introduced into it through an opening. The various stages in the decomposition could also be easily watched through the mica plates.

The salt, when heated at temperatures ranging between 220° and 250° , fused, evolving red fumes. The gas which was collected in the reservoir of the pump was completely absorbed by a solution of ferrous sulphate, thus proving it to be nitric oxide. The residue solidified into a hard lump, consisting of a mixture of metallic silver and its nitrate. So far as this experiment goes, Divers' results are confirmed. The silver nitrite breaks up according to the equation $2\text{Ag}\cdot\text{NO}_2 = 2\text{Ag} + \text{N}_2\text{O}_4$ (1); at the same time, a portion of the silver thus set free acts upon the nitrous fumes, giving rise to silver nitrate and nitric oxide $\text{Ag} + \text{NO}(\text{NO}_2) = \text{AgNO}_3 + \text{NO}$ (2).

The β -Variety of Silver Nitrite.—The silver nitrite as prepared above is dissolved in boiling water, and from the hot saturated solution the nitrite is allowed to crystallise; when the mother-liquor becomes lukewarm, it is decanted into a shallow evaporating dish. When left over-night, slender needles are formed, which are drained and dried as above.

The heating was effected at exactly the same temperatures as in the preceding experiment, namely, between 200° and 250° . Very slight red fumes were noticed, and the substance did not fuse. The gas collected was not absorbed or coloured by a solution of ferrous sulphate, but was completely absorbed by a solution of alkaline pyrogallate, thus proving to be oxygen. As the salt did not fuse, the filamentous character of the original crystals was kept intact; the residue, on treatment with hot water, did not give the faintest opalescence with hydrochloric acid, and, when struck with a hammer, it solidified into a shining regulus of metallic silver.

The results are noteworthy in more respects than one. In the present instance, any formation of silver nitrate is out of the question. This salt is a stable compound, and it decomposes only slightly even at 444° (Divers, *Trans.*, 1899, lxxv., 83). It cannot therefore be urged that a little silver nitrate is at first formed, which breaks up and yields oxygen according to the equation $2\text{AgNO}_3 = 2\text{Ag} + \text{N}_2\text{O}_4 + \text{O}_2$.

The oxylc constitution of silver nitrite, however, often

an easy explanation. Under the action of heat, the scission takes place as indicated by the dotted lines: $\text{Ag}-\text{O}-\text{NO}$.

Thus, from every two molecules of silver nitrite two molecules of nitric oxide and one molecule of oxygen are simultaneously set free. Now, although a mixture of these two gases in this proportion probably gives rise ordinarily to the peroxide, when it is rapidly drawn through or shaken up with a solution of caustic potash, the whole of the oxygen is not fixed, and a portion of it escapes uncombined. In short, the success of Gay-Lussac's method of preparing potassium nitrite is based on this fact (*Trans.*, 1899, lxxv., 85).

It is also remarkable that although a slight quantity of nitrous fumes was noticed, not a trace of silver nitrate was formed under the conditions present. Some dozen experiments were performed with samples of silver nitrite from separate preparations confirming the above results. We give below the result of one typical experiment.

0.43 grm. of salt gave 0.3 grm. of silver and 35.2 c.c. of moist nitrogen (extracted from the alkali in the spiral) at 32.5° and 754 m.m. Found $\text{Ag} = 69.76$, $\text{N} = 8.70$; calculated $\text{Ag} = 70.13$, $\text{N} = 9.09$ per cent.

(The percentages of nitrogen and silver found are rather low, but it should be remembered that the crystals, from the method of preparation, necessarily contained a trace of included mother-liquor).

The ratio of nitric to nitrogen was as 5:3.8. The oxygen collected was 2.6 c.c. at the above temperature and pressure.

(If the whole of the oxygen were absorbed, the alkali, on examination, would have yielded nitric and nitric nitrogen in equal quantities. A few experiments with lead nitrate under conditions exactly similar to the above were made, the only difference being that the substance was heated to a much higher temperature. The mean of three experiments gave the percentage of nitrogen as nitrate = 4.21, as nitrite = 4.21, whilst the percentage of oxygen was 4.6. According to the equation $\text{Pb}(\text{NO}_3)_2 = \text{PbO} + 2\text{NO}_2 + \text{O}$, these proportions should be $\text{N} = 8.48$ and $\text{O} = 4.84$. Hence it is clearly established that nitric peroxide, even when mixed with oxygen, in reacting on an alkali, yields the nitrate and nitrite in equal amount, the oxygen passing off unabsorbed. A trace of a higher oxide of lead which is found in the intermediate stage in the residue appears from its colour to be red lead (compare Divers, *Trans.*, 1899, lxxv., 84). These experiments also prove the trustworthiness of the method employed).

In conclusion, the authors wish it to be distinctly understood that a sharp line of demarcation cannot always be laid down between the fusible and the infusible varieties. As a result of experience gained during the course of several dozens of preparations, it has been found that even under exactly similar conditions the α -variety often turns out to be largely admixed with the β -variety; but the evidence of the formation of the latter in the pure state has been unmistakable.

It is to be hoped that further light will be thrown on the constitution of silver nitrite by the determination of specific gravity, as also by interaction with ethyl iodide.

*203. "The Products of Heating Silver Nitrite." By EDWARD DIVERS.

One of the purposes of this paper is to show that Rây and Gañguli, in the course of their interesting work on the effects of heating silver nitrite, have met with nothing which supports the belief that there are two chemical varieties of that salt. The other purpose of the paper is to endeavour to increase the confidence in the accuracy of their important experimental results, which are hardly in accordance with current views concerning the oxides of nitrogen.

Accounts of experiments on the effects of heating silver nitrite already published will be found in the following publications (*Trans.*, 1871, xxiv., 85; *Proc. Roy. Soc.*,

1871, xix., 429; and *Trans.*, 1885, xlvii., 634; and 1899, lxxv., 111). Precipitated and washed silver nitrite seems always to give some nitrate when heated, but, according to Rây and Gañguli, fractional re-crystallisation of the precipitated salt, effected by dissolving it in hot water and slowly cooling, gives as the last fraction crystals which may be so heated as to decompose without yielding any nitrate at all. The term fractional crystallisation is here used as appropriate, because the authors state that the salt before re-crystallising often behaves as though it were a mixture of its two forms, that which does not give nitrate and that which does, although on what grounds it is difficult to understand. They seem to have made no inspection of the precipitated salt under the lens, in order to seek for two forms of crystals. No distinction can be made as regards any essential difference between "a mealy crystalline powder" and "slender needles," since the former is only the result of hasty crystallisation during precipitation, and the latter are only obtained by slow crystallisation. The former variety of the salt, we are told, fused when heated at 220° and above; the latter variety did not in the least fuse. This statement cannot, however, be accepted as evidence, since silver nitrite does not fuse, but decomposes freely at about 180°, and will do so quickly and completely at that temperature without any fusion of its products of decomposition taking place. What does fuse in the decomposition of silver nitrite at 220–250° is any silver nitrate produced, this salt melting below 217°.

The remaining difference observed in the nature of the decomposition products of the two forms of silver nitrite supplies, however, no grounds whatever for stating, as Rây and Gañguli have done, that the essential or primary decomposition is into silver and nitric peroxide, in the one case, and into silver, nitric oxide, and oxygen in the other, since in this instance the one volume of oxygen and the two of nitric oxide will soon become nitric peroxide also. All that these authors can look to as marking the distinction which they believe to exist, is that they get, exclusive of products common to the two cases, some nitrate and some residual nitric oxide in the one case, whilst in the other, under the same conditions of procedure, they get paler gases, and can isolate from them a little oxygen.

There is not much difficulty in finding a sufficient reason for this difference of behaviour in the different way in which the salt will pack itself in the tube in the two cases. When the salt is heated in the state of powder, the resulting gases will be temporarily imprisoned in the interstices of the mass and the heat will penetrate it slowly enough to permit of the metallic silver of the already decomposed part being acted on by the gases evolved from the still decomposing parts of the nitrite. In this way nitrate will be formed and the gases made to contain a greater proportion of nitric oxide than would otherwise be the case. If, too, it be assumed that the gases are primarily oxygen and nitric oxide, their detention in the residual mass will give time for their union, more or less, into nitric peroxide, and thus account for the redder colour of the resulting gases. On the other hand, when the nitrite is in the form of slender needles, the slight contact of the needles with each other and with the walls of the tube, together with their open arrangement in the tube, will cause the whole mass of the salt to be decomposed so quickly and so nearly simultaneously by the heat suddenly radiated on it from the walls of the heating chamber employed, that, with the vacuum maintained, there will be no temporary detention of the gases by the solids, and no time, therefore, for secondary actions to take place. Not even the production of much nitric peroxide by the union of the oxygen with the lower oxide of nitrogen should be possible before the gases have reached the potassium hydroxide solution.

Rây and Gañguli attempt to strengthen their position that there are two constitutionally different silver nitrites by claiming that, in conjunction with Sen, one of them has shown already (*Trans.*, 1903, lxxxiii., 491) that the decomposition of mercurous nitrite by heat indicates that

being greatly influenced by the solvent used. When ethyl alcohol is employed as the solvent, the reaction becomes unimolecular, and the velocity constant is approximately proportional to the change of temperature. The velocity constants of the reactions between the carbimide and fourteen alcohols are compared.

*207. "The Liberation of Tyrosine during Tryptic Proteolysis." (A Preliminary Communication). By ADRIAN JOHN BROWN and EDMUND THEODORE MILLAR.

A method of directly estimating tyrosine by bromination recently described by James H. Millar (*Trans. Guinness Research Laboratory*, 1903, vol. 1., Part I.) appeared likely to furnish a means of measuring the activity of proteolytic change in those cases in which tyrosine is liberated during the breaking down of the protein molecule. An investigation in this direction was therefore commenced by the authors and the following is a summary of the results so far obtained.

1. J. H. Millar's method of estimating tyrosine by bromination is applicable to the estimation of tyrosine in the presence of proteins and their earlier cleavage products due to enzyme action if suitable control experiments are employed.

2. Tyrosine is not a late product of tryptic proteolysis, as is usually supposed; on the contrary, the tyrosine nucleus of a protein is attacked, and the whole of the tyrosine liberated during the first stage of tryptic digestion.

3. The resistance of the protein tyrosine nucleus to peptic hydrolysis is confirmed.

4. Attention is called to the similarity of Emil Fischer and E. Abderhalden's recent observations on the actions of tryptic and peptic enzymes on polypeptides containing a tyrosine nucleus (*Zeit. Physiol. Chem.*, 1905, xlv., 52) to the authors' observations on the actions of the same enzymes on proteins containing a tyrosine nucleus.

5. The authors' investigations appear to indicate a trustworthy means of differentiating enzymes of a peptic from those of a tryptic nature, and may assist in throwing some light on the confused state of knowledge with regard to the existence of a tyrosine nucleus in the different albumoses resulting from peptic and tryptic proteolysis.

208. "Ethyl Piperonylacetate." By WILLIAM HENRY PERKIN, Jun., and ROBERT ROBINSON.

When piperonylic acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$, is treated with phosphorus pentachloride, it is converted into piperonyl chloride, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{COCl}$, a colourless, crystalline substance which melts at 80° and distils at 155° (25 m.m.). This acid chloride (1 mol.) reacts with the sodium derivative of ethyl acetoacetate (2 mols.) yielding the pale yellow crystalline sodium derivative of ethyl piperonyl-acetoacetate, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{COCNa}(\text{CH}_2\cdot\text{CO})\cdot\text{CO}_2\text{Et}$; the corresponding cupric derivative, $(\text{C}_{14}\text{H}_{13}\text{O}_6)_2\text{Cu}$, crystallises from toluene in bluish-green plates. Ethyl piperonyl-acetoacetate, obtained from the pure sodium derivative by treatment with acids, is a colourless syrup which is soluble in sodium carbonate and gives a reddish-violet colouration with alcoholic ferric chloride.

When the sodium derivative is treated with ammonia and ammonium chloride (Claisen, *Annalen*, 1896, cclxci., 70), it is decomposed with formation of ethyl piperonylacetate, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, a solid, crystalline substance which melts at 41° , gives a reddish-violet colouration with ferric chloride, and yields a copper derivative, $(\text{C}_{12}\text{H}_{11}\text{O}_3)_2\text{Cu}$.

The authors wish to reserve, for a short time, the investigation of these new compounds.

(To be continued).

INSTITUTE OF CHEMISTRY DINNER.

THE Dinner of the Fellows and Associates of the Institute of Chemistry, was held at the Whitehall Rooms, Hotel Metropole, on Monday, the 11th inst., the President, Mr. DAVID HOWARD, in the Chair.

Owing to the dense fog which prevailed, a number of distinguished guests, including Lord Reay, Mr. Justice Buckley, Mr. Justice Swinfen Eady, Professor Meldola (President of the Chemical Society), and Sir R. Douglas Powell, Bart. (President of the Royal College of Physicians), were unable to attend.

Those present included: Sir Thos. H. Elliott, Secretary of the Board of Agriculture; Sir Henry W. Primrose, Chairman of the Board of Inland Revenue; Sir Thos. Pittar, Chairman of the Customs Establishment; Sir William Ramsay, Sir Thos. Stevenson, Sir A. R. Binnie, President of the Institution of Civil Engineers; General J. H. Jeffcoat, Master of the Society of Apothecaries; Mr. John Tweedy, President of the Royal College of Surgeons; Mr. J. Gavey, President of the Institution of Electrical Engineers; Dr. Edward Divers, President of the Society of Chemical Industry; Mr. Edward J. Bevan, President of the Society of Public Analysts; Mr. R. A. Robinson, President of the Pharmaceutical Society of Great Britain; Professor W. A. Tilden, Professor J. Millar Thomson, Sir W. H. Bell, Mr. H. H. Cunynghame, Assistant Under-Secretary of State, Home Office; Mr. W. R. Bousfield, K.C., M.P., Mr. J. M. Astbury, K.C., Mr. A. Gordon Salamon, Hon. Treasurer; Dr. F. Gowland Hopkins, Dr. J. A. Voelcker, Lieut.-Colonel Charles E. Cassal, Dr. W. Kellner, Mr. C. E. Groves, Mr. T. Fairley, Mr. W. W. Fisher, Mr. George Beilby, Mr. Bertram Blount, Mr. Otto Hehner, and Mr. Richard B. Pilcher, Registrar and Secretary.

The loyal toasts having been honoured, Professor J. MILLAR THOMSON proposed "The Houses of Parliament," and alluded to the employment of professional chemists by the various departments of State. In responding, Mr. Bousfield, K.C., M.P., said that, although the Government had done much to foster technical education, there was still much to be done in the promotion of research. We had advanced a good deal in our ideas of what the State should do for science, but not enough so far as the higher walks of it are concerned.

Mr. R. A. ROBINSON, in proposing "The Institute of Chemistry of Great Britain and Ireland," said that it was a great pleasure to him as President of the Pharmaceutical Society of Great Britain to have an opportunity of congratulating the Institute on having attained its present important position. The Institute had nearly 1200 Fellows and Associates, and was doing an important public work in carrying out the objects of its charter, namely, "To promote the better education of persons desirous of becoming public and technical analysts and chemical advisers on scientific subjects; to examine candidates and to grant certificates of competency; and to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency, and by insisting on the observance of strict rules in regard to professional conduct." As an instance of the success it had attained in promoting these objects, he mentioned that 93 per cent of the Public Analysts under the Sale of Food and Drugs Acts were Fellows of the Institute.

THE PRESIDENT, in reply, said that he had been intimately connected with the Institute from its foundation in 1877. They started with a very high ideal. They wished to raise the status of the professional chemist to something like the level of other learned professions. To-day, the position of the professional chemist was higher in England than elsewhere, because there was more independence of thought, and that individual excellence and individual devotion to duty which was required in a true professional spirit. He viewed with great apprehension the increasing desire for cheapness. It was quite true that you could get

Royal Institution.—On Thursday next, December 28, at 3 o'clock, Professor H. H. Turner will deliver the first of the Christmas Course of Six Illustrated Lectures, adapted to a juvenile auditory, on "Astronomy."

work done cheaper wholesale than retail, but it was not in the mass that they got the intelligent progress that was wanted. He earnestly hoped that the temptation to cheapness would not be allowed to enter professional scientific questions. The examinations of the Institute were attended now by over 100 Candidates yearly, and arrangements were being made for the conduct of examinations in the Colonies. He also alluded to the new scheme of Examinations in Technical Chemistry which the Institute will put into operation next year.

Sir THOMAS STEVENSON proposed the toast of "The Learned Societies and Institutions," which was acknowledged by Mr. TWEEDY and Sir A. R. BINNIE.

Sir WILLIAM RAMSAY proposed "The Guests." Sir THOMAS H. ELLIOTT and Mr. ASTBURY responded, and the proceedings terminated.

FARADAY SOCIETY.

Ordinary Meeting, October 31st, 1905.

Lord KELVIN, President, in the Chair.

PROF. ERNEST WILSON, gave a *résumé* of his paper on "Alternate Current Electrolysis," which had been taken as read at the previous meeting. (See CHEMICAL NEWS, vol. xcii., p. 198).

Mr. W. R. COOPER then read an abstract of his paper on "Alternate Current Electrolysis as shown by Oscillograph Records," illustrating his remarks by projecting on the screen a selection of his photographic records.

It is pointed out that although polarisation is of the nature of capacity in an alternate current circuit, there is a considerable difference. What might be termed the E.M.F. of a condenser rises and falls as rapidly as the applied pressure, but although the E.M.F. of polarisation may rise as rapidly as the applied pressure, it falls more slowly, with the result that, under suitable conditions, the current curve may depart very considerably from the sine form. Actual oscillograph records are reproduced in support of this view. In considering the subject it has been very generally assumed that the current follows a sine curve. Since the curve obtained depends very much on the conditions of the experiment, it is necessary to define the conditions very carefully before conclusions can be drawn from different experiments. Oscillograph records of electrolytic rectification were also shown.

Mr. A. E. TROTTER referred to the bearing of work on alternate current electrolysis on the corrosion of water and gas pipes caused by stray currents from alternate current systems. He described some practical experiments he had made with lead pipes buried in the earth; these experiments showed that there was a minimum current density or a minimum voltage—he was not sure which—below which no corrosion took place. More work was required to be done in order to indicate the exact conditions necessary for corrosion, but great caution was necessary in the application of scientific experiments to practice.

Mr. J. SWINBURNE thought that the greater absorption of energy found by Professor Wilson at the lower frequencies was simply due to diffusion, and this was borne out by Mr. Cooper's curves.

Dr. F. MOLLWO PERKIN said he had found that platinum plates electrolysed alternately in dilute sulphuric acid were more corroded at low than at high frequencies; a colloidal solution of platinum seemed to form, and the electrodes had an etched appearance.

Professor A. K. HUNTINGTON contributed a "Note on the Crystalline Structure of Electro-deposited Copper," which was illustrated by photomicrographs of sections of the deposits referred to in the paper.

In Mr. Cowper-Coles's process for making copper-wire electrolytically, a spiral scratch or groove on the mandril causes the copper deposited on it to part so easily that a long ribbon can be obtained. The author's explanation is

that the direction of the lines of crystallisation of an electro-deposited metal are the same as in a casting made on surfaces having the same inclination, i.e., the crystals form at right angles to the surface on which the deposit or the casting is made. It follows that when the crystals which form on surfaces more or less at an angle to one another meet, there will be want of continuity in the two sets of crystals, and a line of weakness will be developed. Therefore in castings and deposits when strength and not rupture is aimed at, it is important to avoid sharp angles. In the case of a cathode plate which has been deposited on a thin strip of electro-deposited copper, the crystals of the original strip continued in some cases in the cathode plate. On annealing the electro-deposited copper the long crystals of the deposit are completely broken up and become largely twinned. Hence brittleness due to the direction in which crystals form in castings and electro-deposits may be modified and probably completely removed by suitable annealing, unless the continuity is entirely broken.

Mr. J. F. R. RHODIN thought that structure of the copper deposited in a groove, such as Mr. Cowper-Coles employed, depended on electrostatic repulsion rather than on crystalline form. The fringing at the edge of a deposit, even where the current density was not high, seemed to him to him to confirm that explanation.

Mr. W. POLLARD DIGBY's paper on "Some Observations respecting the Relation of Stability to Electro-chemical Efficiency in Hypochlorite Production" was taken as read.

The author commenced by drawing attention to the fact that in all electrolytic methods of producing hypochlorite solutions, only a small portion, rarely more than 18 per cent of the chlorine usually present in the form of chloride, is converted into hypochlorite, and suggests that the amount of available chlorine produced from a sodium chloride solution depends upon the relation which the amount of unconverted sodium chloride actually present between the electrodes bears to the current density. As regards stability, particulars are given of two tests in which the rate of depreciation, although only 0.3 to 0.4 grm. in twelve hours per litre for solutions containing 8 grms. of available chlorine per litre, caused a very great depreciation in the yield per kilowatt hour supplied. The suggestion is advanced that no test of the efficiency of any apparatus for the electrolytic production of the hypochlorites can be regarded as complete without an estimation of the losses through instability, and a mention of the volume of the contents of the electrolysis tank. While stability of solution does not greatly affect the efficiency of any continuous type of apparatus (in which the sodium chloride is fed in at one end and drawn off at the other end ready for continuous use), it will materially affect the efficiency in any non-continuous apparatus, or in any apparatus in which the electrolyte is circulated through an external cooling tank and returned to the electrolyser to be further worked up. It is suggested that the presence of minute quantities of iron in the solution have also a bearing on the depreciation.

MEETINGS FOR THE WEEK.

THURSDAY, 28th. } Royal Institution, 3. (Christmas Lectures,
SATURDAY, 30th. } adapted to a Juvenile Auditory). "Astronomy,"
by Prof. Herbert Hal Turner, D.Sc., F.R.S.

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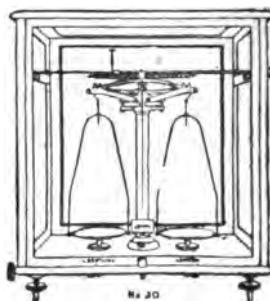
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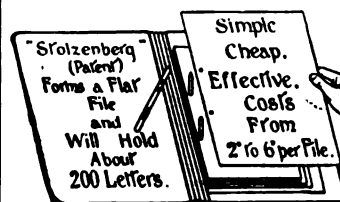
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THE CHEMICAL NEWS.

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ETCHING WITH HYDROFLUORIC ACID.

By NICHOLAS KNIGHT.

IN the interesting and practical experiment of etching on glass with fluor-spar and sulphuric acid, it is desirable to have both the surfaces of the glass coated with a thin layer of wax or paraffin; otherwise the upper surface becomes etched by the acid fumes, and the experiment is thereby marred. To obtain the desired effect, the writer for a number of years has kept an ordinary copper water-bath, 6 inches in diameter, nearly filled with paraffin. This is carefully heated to avoid burning until it is all melted. The glass object upon which the etching is to be made is immersed in this liquid and quickly withdrawn, when both sides and the ends as well are covered uniformly with a thin layer. After the etching is accomplished, the paraffin is easily removed by immersing the glass in warm water, not sufficiently hot to break it. The usual way of spreading the paraffin on one side of the glass by warming it with a small flame underneath often fractures the glass, but by the method described in the foregoing the etching is so easily and satisfactorily made that the students are eager to repeat the experiment, and they etch beautiful monograms and designs on various objects—watch-crystals, drinking-glasses, paper-weights, and similar articles. In this way there is a perpetual reminder of the days spent in the fascinating realms of experimental chemistry.

Cornell College, November 28, 1905.

THE PHYSICS OF ORE FLOTATION.*

By J. SWINBURNE and G. RUDORF, Ph.D., B.Sc.

(Concluded from p. 289).

RETURNING to the ores, the various sulphides have different adhesions. The gangue, as a rule, has very great adhesion, and cannot be floated. Even such bodies as stibnite, unless very finely ground, have too much adhesion to be floated at ordinary temperatures. The adhesion is altered enormously with change of temperature, however. This is well known in the case of taking out spots of grease from clothes. If the cloth is ironed with blotting-paper underneath it, the grease will run from the hot cloth into the cooler blotting-paper. In the same way, cloth that seems dry when cooled seems damper when warmed, as the adhesion or capillary attraction is reduced. A thick piece of dry bread when toasted gets quite moist in the centre, partly because the water has moved in from the outside, which is hotter than the inside, and partly because the adhesion is less. In the case of ores, many of the sulphides, such as galena, stibnite, and molybdenite, have their adhesion reduced enough to be floated easily near the temperature of boiling water, and though the surface tension is also reduced with increase of temperature, the adhesion is reduced much more quickly. The surface tension becomes zero at the critical temperature; the adhesion probably falls to a very low value at the boiling-point.

In order to get concentration by flotation, it is necessary to have an ore whose valuable constituent is some "greasy"

sulphide,* such as galena, or at most so automatically attached to the greasy sulphide that it comes off with it. Zinc sulphide is thus easily raised by galena when intimately associated, as in the Broken Hill and some of the Vieille Montagne Company's ores.

It is not enough to have the greasy particles; it is necessary to produce the gas-bells and get them against the particles. In practical work the only gas that comes off is carbon dioxide, and this appears to come largely from calcite. But mixing calcite with an ore which has a greasy constituent will not necessarily float it; the gas is apt to come away from the particles of calcite without getting attached to the ore. It seems much more likely that the gas that really effects the flotation is generated by the action of acid on small quantities of carbonates produced by a slight weathering of the ores. It is most likely due to small amounts of carbonate of iron and manganese. These carbonates are also not attacked by dilute acid in the cold.

But there is another consideration. The question of adhesion and of formation of adherent gas-bells is intimately connected with the air-film. Most, if not all, substances condense a volume of air or water, or both, on their surfaces. An extreme case of this is the absorption of hydrogen gas by palladium. No compound is formed here, because, according to Roozeboom, the amount of gas absorbed at any particular temperature is *not* constant, but varies with the pressure. Other elements, e.g., vanadium, nickel, and copper, also absorb small quantities of hydrogen, but in no case does the amount of gas absorbed bear any simple atomic ratio to the amount of metal. Thus vanadium absorbs 1.3 per cent of its volume of hydrogen, electrolytic zinc a few hundredths of 1 per cent, copper wire 0.306 vol., ordinary porous nickel absorbs 165 vols. of hydrogen, but loses it again in two to three days, and so on. These solid solutions, occlusions, or condensations, whatever they may be, must be carefully distinguished from the true hydrides, such as those of the alkali metals. The condensation of gases on solid surfaces and the great persistence of the film is especially familiar to workers with high vacua. A glass bulb, for instance, on exhaustion keeps on giving off gas for days. If the bulb is heated as strongly as the glass will bear, the gas comes off much more quickly. A Ruhmkorff discharge also brings it off. If the bulb, while still exhausted, is washed or filled with mercury, it will sweep the gas off the glass ("Incandescent Lamp Manufacture," *Electrician*, 1887). The electrodes also give off gas on sparking the tubes, and this gas cannot be got rid of by exhausting the tubes. Very many observers have noticed and described this nuisance. Aluminium is especially obstinate as shown by the experiments of Callendar. The literature is to be found in Kayser's "Handbuch des Spektroskopie," vol. i., pp. 239-243. This air-film seems to be intimately connected with the small adhesion for water. It may be that the air-film is itself the result of adhesion for gas, which is able to condense the gas on the surface. It cannot be any simple action of that sort, however, for time has great influence. Thus the gas comes off the inside of the exhausted globe very slowly, as already mentioned. On the other hand, small metal objects will float on water. Interesting experiments in this direction are recorded by Mayer (*Science*, 1896, [2], iv., p. 298). He floated rings of various metals—aluminium, iron, tin, brass, copper, lead, and German silver—made of 1 m.m. diameter wire and 50 m.m. in diameter, on water. The metals, however, must be clean and dry. If, after one of these rings has been sunk in water, it be dried and the experiment repeated, it will be found impossible to float the ring. After leaving it in the air for half-an-hour or so, it can be

* This effect of greasiness was well shown by the following experiment. Some ordinary steel filings, which probably had some oil on their surface, were immersed in dilute acid. Hydrogen was evolved round the particles, which were kept dry by the oil, large bubbles rose to the surface and burst, leaving absolutely dry filings on the top of the liquid. Clean new filings did not show this phenomenon.

* A Paper read before the Faraday Society, December 12, 1905.

again floated. Similarly a heated platinum ring will not float immediately after cooling, but will do so after lying in the air for a short time. This shows that the film takes time to form. Another way of demonstrating the presence of the gaseous envelope is to shift some powdered substance which easily sinks, such as sand or ferrous sulphide, on to the surface of hot water, previously freed from gas by boiling. Bubbles of gas rise from the surface of the solid particles.

Many observers have recorded the floating of perfectly dry sand on water. Among these may be mentioned Simonds (*Amer. Geol.*, 1896, xvii., 29; and *Science*, 1900, [2], xi., 510), Ladd (*Amer. Geol.*, Nov., 1898), Graham (*Am. Journ. Sci.*, 1890, [3], xl., 470), Nordenskiöld (*Nature*, 1900, lxi., 278), Carus-Wilson and Evans (ii., p. 318), and perhaps others. Evans also found that pieces of slate $1.5 \times 0.75 \times 0.1$ c.m. float on tap-water, if perfectly dry.

According to Simonds, the floating of the sand depends on the shape of the grains. Ladd notes the same condition, and adds that the pieces must be sharply angular. Felspar and mica will also float under these conditions.

Spring (*Bull. Soc. Belg. de Geol.*, 1903, xvii., 13) has made some experiments on the wetting of sand, and finds that it depends chiefly on the capillary-constant of the liquid and on the fineness of the particles.

However, the substances usually known as gangue are much more easily wetted than the metallic substances. Again, some are much more easily wetted than others. Thus, iron pyrites is easy to wet; that is to say, difficult to float, whereas antimony sulphide is difficult to wet, or easy to float.

A particle which is once wetted will never float, because even if a gas bubble were formed on or round it, it would not carry the solid up, as it falls through. On the other hand, if a particle has still a very thin film on it, but this is insufficient to buoy it up, it is easily conceivable that by generating gas, such as CO_2 , upon it, this gas will add itself to this small air-film and eventually raise the particle. Here, again, the temperature seems to be of importance, and this probably explains why a substance like ferrous carbonate, which is not attacked by dilute acid at a low temperature, is better than calcite or copper carbonate which are attacked in the cold.

Nothing is known about the thickness of the air-film or whether it is the same for all substances; or, as is more likely, variable. But it is very probable that for a given substance the thickness of the film is the same whatever the size of the particle; hence, only small particles can be raised without the addition of some other gas, such as CO_2 .

That the air does play an important part is shown in the case of stibnite and molybdenite. They can be concentrated by placing the ore in water nearly boiling. Apparently there is enough air on the surface of the particles to form with the steam a bell consisting of air and steam, which floats the particle. The air-film, or a surface with small adhesion, also gives a bell of gas or of steam a chance of forming. The surface tension makes it impossible for a bell of steam to start, as the bell is under extra pressure due to the surface tension, the pressure of the contained gas varying inversely as the diameter of the bell. Thus a bell of air, at ordinary temperatures, of 0.01 m.m. diameter has an extra pressure on it of 30,000 dynes per square centimetre, equal to a head of about 30 centimetres of water. The explanation we offer—and it seems sufficient for the Potter process—is, therefore, that all solids have on their surface when dry a thin film of gas, probably air. Some of them—such as sand, quartz, carbonates—easily give up this film in water and become wet; whilst others, such as most metallic bodies, and especially the sulphides of lead, molybdenum, and antimony, have a smaller tendency to part with the film, and are not easily wetted. These can, therefore, be floated. If the air-film is insufficient to raise the particle, the flotation can be increased by the slow generation of gas on the particle. But if the particle has

once lost its air-film, that is to say, got wet, it can never be raised, and no amount of gas generated on it can help matters.

To sum up, we would suggest that the selective flotation is due to the presence of "greasy" sulphides, which have small adhesion, and that a high temperature is necessary to reduce the adhesion enough for the bells of gas to stick. It seems necessary that the gas should be produced at the surface of the particles themselves; and it is, in fact, produced by the decomposition of carbonates due to slight weathering of the ore. If an ore that can be floated is treated with acetic acid to remove the traces of carbonate, it cannot then be floated again. The air-film also plays an important part; and if an ore is thoroughly washed or boiled in water to remove the air-film, it cannot be concentrated with acid. Some ores, such as stibnite and molybdenite, appear to have enough air on their surface to form a mixture of air and steam at a temperature below boiling point, which has enough volume to float the particles. Acid is therefore unnecessary in such cases. Of the various ores and sulphides we have tried in dilute acid or acid sulphates of soda, the following are most easily floated in order of merit:—

Molybdenite.

Stibnite.

Galena.

Mixed zinc-lead sulphides, such as the Broken Hill ores.

Copper glance.

Zinc blende.

Iron pyrites.

The last two scarcely float at all. Copper glance only floats if slightly weathered, and then only in very small amounts.

With the Broken Hill ores the ratio of the Zn : Pb in the concentrate differs very little from that in the ore, only the gangue being left behind. Galena is fairly easy to float if finely ground, but owing to its rather high specific gravity very fine pulverisation is necessary to float it successfully. Stibnite and molybdenite go quite easily owing to their very greasy nature.

We have made a good many experiments with various ores, but do not think it is necessary to go fully into them here. We have therefore only given this short list as an example of the way in which things go.

We also tried some of the gangue obtained from the Broken Hill ores by the Phoenix process due to one of us. This looks like river-sand, and consists principally of rhodonites and garnets. Not the slightest flotation was obtained.

It is interesting to note that ground malachite—copper carbonate—floats fairly well in water. It may be remembered that this mineral has a peculiar greasy feeling. Beyond this, we have not found any other carbonates that float.

This list is only roughly correct, however, and it is most probable, in fact almost certain, that various samples of sulphides differ considerably; and if a slight weathering is necessary to produce the small trace of carbonate needed to give flotation, the "greasiness" in itself is not sufficient to give the separation. It is, in fact, quite impossible to tell beforehand which ores can be separated by flotation.

We have not gone much into the question of merits of the various solutions used for concentration by flotation. Potter originally used dilute acid, preferably sulphuric, of about 2 per cent strength. A saturated salt-cake solution is employed by another inventor, Delprat.

We have found that generally the latter solution works rather better than the former, and it has been suggested that this is due to the isohydric influence of the sodium sulphate on the sulphuric acid, thus driving back the dissociation of the latter, so that a saturated solution of salt-cake acts as a weaker acid than the dilute sulphuric acid itself. This is, however, not the case for several reasons:—

—1. The saturated salt-cake solution conducts considerably

better than the dilute acid. 2. It acts more violently on carbonates and iron than dilute acid. The degree of dissociation is, no doubt, considerably driven back, but as the total concentration in one case is so much greater than in the other, the actual concentration of the hydrogen-ions need not be less. In fact, it is only necessary to assume that the salt-cake solution is dissociated to about 5 per cent to make the H-concentration the same as that in 2 per cent acid where the dissociation is probably complete, or, at any rate, nearly so. All this is assuming there are such things as ions. With salt-cake solution the bubbles get larger than with dilute acid and rise more slowly owing to the greater density and viscosity of the former solution. Certainly a much more stable and compact scum is formed when salt-cake solution is used, and this is no doubt due to the viscosity of this solution, but more especially to the surface viscosity, which is always greater than the ordinary viscosity or internal friction. It is well known that bodies on the surface of a liquid attract one another if all be wet or all be dry. The former case does not concern us, as it only applies when the solid is lighter than the liquid. If one particle be wet and another dry then there is repulsion between them. The compactness of the scum in the case of salt-cake solution is therefore most likely due to the fact that the particles, on account of the increased surface viscosity as compared with dilute acid, tend to keep drier than with the dilute acid, and therefore attract one another, forming a compact scum. It need hardly be pointed out that this apparent attraction is really a surface tension phenomenon again. If particles of dry sand rest on water, each produces a little dent in the surface, and increases its area. The increase of area of the tense surface is least when the particles are altogether, making one big dent. This holds good—to a less extent—with greasy particles floating and with completely wet particles. With wet particles the dents become prominences, but the surface action is otherwise the same.

As regards the actual values of the surface tensions of water, dilute acid, and saturated salt-cake solution, there is very little difference. Dilute 2 per cent sulphuric acid has the surface tension very little smaller than that of water, and the same can be said of the salt-cake solution. The temperature coefficient for water and dilute acid is about the same. It is given by the formula $T_t = T_0 - 0.002t$. For salt-cake solution, the coefficient is practically zero. We have tried no other solutions, and are therefore not in a position to give any general explanation for the behaviour of various solutions. All we have tried to do is to sketch a rough explanation dealing broadly with the physics of ore flotation.

We are indebted for many facts to Mr. Blount and Prof. Huntington, who have both given much attention to the flotation of ores.

Study of an Industrial Cuprosilicide.—Paul Lebeau. —M. Vigouroux, in 1896, prepared a compound of copper and silicon by heating a mixture of the two elements containing 10 per cent of silicon, the composition corresponding to SiCu_2 . In 1901, he obtained an ingot containing less than 5 per cent. The author in his researches on metallic silicides used an industrial silicide of copper containing 50 per cent of silicon, and after describing the appearance and chemical properties he comes to the conclusion that the limit of combination of copper with silicon is not represented by SiCu_2 , but approaches to the formula SiCu_4 containing 10 per cent of combined silicon. He is curious to know how the siliciuration of copper varies with different conditions and proposes to continue his investigations. *Comptes Rendus*, cxli., No. 22.

Erection of Steel Chimneys.—Thomas Piggott and Co., makers of pipes, tanks, and steel structures, have just successfully completed two steel chimneys in South Wales, one 175 feet high and the other 125 feet high.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 7th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

(Concluded from p. 293).

209. *The Action of Ultra-violet Light on Moist and Dried Mixtures of Carbon Monoxide and Oxygen.* By SAMUEL CHADWICK, JOHN EDWIN RAMSBOTTOM, and DAVID LEONARD CHAPMAN.

The chemical effects produced by the passage of the electric discharge through gases are the result of at least three distinct causes, namely, (1) the cathode rays, (2) ultra-violet light, (3) catalytic action of the electrode and in particular the cathode. Ultra-violet light alone has been shown by Leonard to act on oxygen with the formation of ozone. The authors working with a quartz mercury lamp, with which 3 per cent of ozone could be produced from pure oxygen, have obtained the following results. A mixture of equal volumes of carbon monoxide and oxygen dried with sulphuric acid and submitted to the action of ultra-violet light, contracted at first slowly, and then more rapidly, until a maximum rate of decrease of volume was attained. The rate of contraction then gradually decreased, and finally became so slow that the experiment was stopped, and the composition of the gases found by analysis. It was ascertained that 22.95 per cent of the carbon monoxide had been converted into carbon dioxide, and that 39.63 per cent of the original oxygen had been changed into ozone.

A mixture of equal volumes of carbon monoxide and oxygen dried with phosphoric oxide behaved in almost the same way as the mixture which had been dried with sulphuric acid alone. When the contraction had reached approximately the same value as in the last experiment, it was found on analysis that 19.42 per cent of the total carbon monoxide had been converted into carbon dioxide, 37.48 per cent of the original oxygen being this time changed into ozone.

With the same mixture saturated with water vapour at 16°, the result was markedly different. The rate of contraction was practically uniform throughout the experiment, and this rate was less than half the value of the maximum rate with the dried mixture. When the total contraction had reached almost the same value as in the two previous experiments, it was found that 53.2 per cent of the carbon monoxide had been converted into carbon dioxide, and only 2.6 per cent of the oxygen into ozone.

If the first action of the ultra-violet light is conceived as consisting of a breaking up of the oxygen molecules into atoms, the atoms of oxygen thus formed prefer to combine with the molecules of carbon monoxide when the gases are moist, but with oxygen molecules when the gases are dry. In the present case, the rate of chemical change, measured by the contraction, is not accelerated by the presence of moisture, but the course of the reaction is determined by the hygroscopic condition of the mixture.

210. *"Benzoyl Derivatives of Salicylamide."* By ARTHUR WALSH TITHERLEY.

Doubt has been thrown by Einhorn and Auwers on the formula $\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{NH}$, attributed by Titherley and Hicks, (*Trans.*, 1905, lxxvii., 1207) to the stable benzoylsalicylamide (m.p. 208°) originally obtained by Gerhardt and Chiozza (*Ann. Chem. Phys.*, 1856, xlvi., 139), and which is produced by rearrangement even at 15° from the labile *O*-benzoylsalicylamide, $\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$ (m.p. 144°), recently isolated by Titherley and Hicks.

Einhorn, in conjunction with Schupp (*Ber.*, 1905, xxxviii., 2792), and also with Haas (*Ber.*, 1905, xxxviii., 3628), considers the stable substance to be the *N*-benzoyl derivative, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHBz}$, as also does Auwers (*Ber.*, 1905, xxxviii., 3256, who regards the rearrangement as due

to the wandering of the benzoyl group from O to N: $\text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$ (labile, m. p. 144°) $\rightarrow$ $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHBz}$ (stable, m. p. 208°). The change would be analogous to that which takes place when attempts are made to isolate O-acyl-o-hydroxy-aromatic amines of the type $\text{AcO}\cdot\text{C}_6\text{H}_4\cdot\text{NHR}$ and $\text{AcO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NHR}$, where rearrangement occurs leading to the production of the N-acyl derivatives.

If the N-benzoyl formula be assigned to the substance (m. p. 208°), it must be looked on as possessing anomalous properties; thus, it gives no ferric chloride reaction, is not decomposed by ammonia, like $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NHBz}$, and in other ways does not behave like an N-benzoyl derivative. Further, on heating with phosphorus oxychloride, it yields benzoylsalicylnitrile, which favours the O-benzoyl formula, thus:



Further investigations are proceeding with a view to elucidating the correct constitution of the substance.

211. "The Constitution and Colour of Diazo- and Azo-Compounds." By ARTHUR HANTZSCH.

In the August number of the *Transactions*, Armstrong and Robertson published a paper under the title: "The Significance of Optical Properties as Connoting Structure" (pp. 1272—1297), in which my theory of the stereochemistry of the diazo-compounds is criticised, and the remarkable conclusion expressed, that the "Hantzsch-Werner hypothesis" (in reality, so far as concerns the diazo-compounds, the "Hantzsch hypothesis"), "besides being an intangible and improbable conception, is unnecessary in fact."

If such an expression of opinion were correct, it would certainly not be without some significance, whilst the same holds conversely if such a view is shown to be incorrect, or at all events founded on a false basis. Since the latter is the case, it will be readily admitted that such a refutation ought also to find a place in the Society's publications.

The facts on which I venture to base this statement are simply the various researches on the subject, which I have published in the pages of the *Berichte der deutschen chemischen Gesellschaft*, a synopsis of which is to be found in a small published brochure, "*Diasoverbindungen*," F. Enke, Stuttgart, 1902.

The delay in replying is due to the fact that I only became acquainted with Armstrong and Robertson's work at the beginning of November.

Armstrong and Robertson proceed from the assertion that "all compounds containing the group $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{X}$ must be coloured" to the conclusion (p. 1280) that "all compounds of the type $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{X}$ should be coloured, and consequently only coloured diazo-compounds can be represented by such a formula. The formula assigned by Hantzsch to the so-called normal and isodiazotates are at once ruled out of consideration by this argument, as both these classes of compounds are colourless;" in other words, the latter do not correspond to the structural formula $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OK}$.

It must first be observed that all chemists from Kekulé onwards, who have worked on diazo-compounds, must therefore have employed an incorrect formula, for they all, before as well as after the discovery of diazo-isomerism, accepted the formula $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OK}$ for at least one of the two isomerides. But apart from this, Armstrong and Robertson's assertion can readily be shown to stand in contradiction to the facts, for according to their views the nature of an azo-compound as such is established by the fact that the compound is a coloured substance, and, conversely, a particular substance cannot be an azo-derivative because it is colourless. Such a conclusion has up to the present proved totally unacceptable, for Thiele's well-known extensive researches (*Annalen*, 1896, ccxc., 1) have shown that both coloured and colourless azo-compounds exist in the aliphatic series; for instance, the deep red azo-dicarboxylic ester, $\text{CO}_2\text{R}\cdot\text{N}:\text{N}\cdot\text{CO}_2\text{R}$, and the colourless azo-

iso-butyric acid derivatives, $\text{CRME}_2\cdot\text{N}:\text{N}\cdot\text{CRME}_2$. When Armstrong and Robinson proceed "being colourless, the diazo-salts cannot be formulated as diazene ($\text{N}:\text{N}$) compounds" (p. 1280), it is certainly logical to assert "that being colourless these so-called azo-compounds of the aliphatic series cannot be compounds of the type $-\text{C}\cdot\text{N}:\text{N}\cdot\text{C}-$."

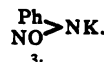
So long, therefore, as Armstrong and Robertson do not offer any explanation of these facts, or substitute other constitutional formulæ for these colourless compounds, regarded generally as azo-derivatives, just so long will their conclusion, namely, "that diazotates being colourless cannot have the ordinary formula $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OK}$," remain unacceptable. But amongst the diazobenzene derivatives there also exist true chemical compounds containing the group $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{X}$; these, therefore, according to Armstrong and Robertson, must be coloured, but in reality they are colourless. For example, amongst the nitro-isodiazobenzene esters we have the nitro-diazo-ester, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{O}\cdot\text{CH}_3$ (von Pechmann, *Ber.*, 1894, xxvii., 672), which, to quote the author's description, "in the pure state is perfectly colourless." Here again it is necessary for them to replace the formula by a more suitable one, or their conclusions must necessarily be regarded as incorrect.

According to their view, "the normal diazotates must perforce be regarded as diazonium derivatives," I do not consider it necessary to disprove this statement, and will content myself by pointing out that even Bamberger has given up the diazonium formula for the labile diazotates (*Annalen*, 1900, cccxiii., 98), and that his last attempt to rehabilitate it (*Ber.*, 1903, xxxvi., 4054) has been shown to be unwarranted (*Ber.*, 1904, xxxvii., 1084).

As regards the proposed formulæ for the isodiazotates (p. 1282), $\text{Ph}\cdot\text{N}-\text{N}\cdot\text{K}$ or $\text{Ph}\cdot\text{NK}\cdot\text{NO}$, the same remarks

apply. I discussed these formulæ at length some considerable time ago, and showed them to be unsatisfactory, and they have, as a matter of fact, been abandoned by all chemists who have studied experimentally the chemical behaviour of these substances. The two formulæ of Armstrong and Robertson also stand in contradiction to the fact that the previously-mentioned diazo-ester, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{OCH}_3$, can be obtained from the isodiazotate, so that in consequence the existence of a third hydroxyl form must be accepted. These hydroxyl compounds ($\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OH}$) are not imaginary tautomeric substances, but real, definite, chemical compounds, for in conjunction with W. Pohl (*Ber.*, 1902, xxxv., 2964) I have shown that from the colourless isodiazotates there is formed, primarily, the free iso-(anti)diazohydroxide as a colourless, true acid, the general behaviour of which certainly indicates the presence of an (OH) group.

Armstrong and Robertson must therefore suggest another "hydroxyl formula" in place of $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OH}$, and the fact cannot be too plainly pointed out that in accepting the nitrosoamine formula for the isodiazotates they again immediately stand in contradiction to their fundamental doctrine on the relation of colour to constitution, for, as is well known, most of the true secondary nitrosoamines, and nitrosoamine derivatives, are coloured. The indifferent primary nitrosoamines obtained as pseudo-acids by W. Pohl and myself through intramolecular charge of the diazohydroxides are also coloured, although as a logical consequence from Armstrong and Robertson's nitrosoamine formula (that is, absence of the group $\text{Ph}\cdot\text{N}:\text{N}$) these isodiazotates should be colourless if they were really nitrosoamine salts. As is seen from the three formulæ:—



by simple substitution of K for H or R, we obtain from the coloured substances (1) and (2) a colourless potassium salt (3), a result which is again incompatible with Armstrong and Robertson's theory.

(The reference to Dobbie and Tinkler's work (*Trans.*, 1905, lxxxv., 277); and *Proc.*, 1905, xxi., 75), namely, "that the salt $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{OK}$, in respect to its absorption spectrum, behaves as a nitrosoamine, and not as a diazo-salt," stands in marked contradiction to all its chemical properties. This being so, too much weight cannot be attached to this evidence until it has been ascertained, for example, how the isomeric esters $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{O}\cdot\text{CH}_3$ and $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)\cdot\text{NO}$ behave under similar conditions, a point which the above-named chemists, at my request, have most kindly promised to investigate).

The whole of Armstrong and Robertson's views on the normal diazosulphonates and diazocyanides are quite incorrect. They state (p. 1281) "the action of sulphite may be supposed to involve in the first place the formation of a diazonium sulphonate, $\text{R}\cdot\text{N}:\text{N}\cdot\text{SO}_3\text{K}$," and, so far as

I can understand, also put forward the formula $\text{Ph}\cdot\text{NH}\cdot\text{SO}_3\text{K}\cdot\text{NOH}$. The latter formula is impossible, because most diazosulphonates correspond to the formula $\text{Ph}\cdot\text{N}_2\cdot\text{SO}_3\text{K}$; that is, to one containing no water. The diazonium formula itself stands in contradiction to their theory, for if the appearance of colour denotes a change in constitution, and if all the sulphonates of colourless metals (namely, those of silver and mercury) are colourless, why is it that the diazonium sulphonates formed from the colourless diazonium and sulphonic acid components possess an intense orange colour? From the very fact that the labile equally with the stable sulphonates are coloured, they must both be azo-compounds, $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{SO}_3\text{K}$.

The statement that "the so-called *syn*-compound sulphonates and cyanides may well be simple equilibrated mixtures of diazonium cyanides and sulphonates with the stable *anti*-compounds" (p. 1283) is controverted by the facts, for all the normal diazocyanides exhibit analogous behaviour with water and cuprous oxide, but in a manner quite different from that of the isodiazo-cyanides. Further, as regards their colour and constitution, the labile *syn*-diazocyanides and diazo-sulphonates are always more intensely coloured than the stable *anti*-forms. All diazonium sulphonates are colourless, and all diazosulphonates should be colourless; so that Armstrong and Robertson's view leads to the remarkable result that, by the addition of a colourless to a coloured substance, the colour intensity of the resulting mixture is increased—certainly the greatest *contradictio in adjecto*. In addition, Armstrong and Robertson have not sufficiently taken into consideration the fact that the labile cyanides are distinct chemical compounds possessing definite unchangeable properties, that is they are not chemical mixtures. The explanation of the change of the *syn*- into the *anti*-form (p. 1281) is impossible by reason of the assumption that an addition of the elements of water takes place, with a subsequent splitting off of the same elements, for in reality many *syn*-sulphonates and very many *syn*-cyanides isomerise in the solid state or in anhydrous solvents.

In short, therefore, the whole of Armstrong and Robertson's conceptions with respect to labile diazo-isomerism are impossible, and their remark that my "*syn-anti*-conception is based upon a false use of the principle of analogy" will certainly be considered as more applicable to their own untenable theories, according to which "the stereochemistry of the diazo-compounds is unnecessary in fact."

With such statements as "in the case of the diazosulphonates, it is clear that they differ essentially in type," put forward without the support of a single experimental fact, equally without any theoretical explanation, discussion is out of the question, and, in fact, would be superfluous.

It is unfortunately necessary for me to make an emphatic protest in reference to Armstrong and Robertson's remarks (p. 1280) on the small value which ought to be placed on the analytical results of the labile diazo-isomerides. One

has the right to expect that before such statements are made reflecting on the accuracy of the work in question, the greatest care has been taken to verify the facts. That such a sweeping assertion is altogether unwarranted will, I think, be admitted from a consideration of the following points:—

1. *Labile Diazotates*.—The labile diazotates certainly always contain small quantities of alkali (*Ber.*, 1901, xxxiv., 2159; 1902, xxxv., 2969), or water of crystallisation (*Ber.*, 1895, xxviii., 2006; 1896, xxix., 1077), but in the form of their crystalline salts they have been obtained quite pure, so that no chemist who has worked on the subject, from Kekulé onwards to Bamberger, has ever seriously questioned the accuracy of the empirical formula ArN_2OK for the diazotates.

2. *Labile Diazosulphonates*.—The numerous concordant analyses on these substances (*Ber.*, 1894, xxvii., 3529; 1897, xxx., 76, 80—81) prove undoubtedly the accuracy of the formula $\text{PhN}_2\text{SO}_3\text{K}$ for this substance. It is true there is generally present a small quantity of the *anti*-salt, formed by spontaneous isomerism of the *syn*-derivative, but this certainly does not come into question as affecting the accuracy of the formula or as regards the facts of the isomerism.

3. *Labile Diazocyanides*.—The fact must be emphasised that many of these compounds can without difficulty be very readily obtained and isolated in a pure state (*Ber.*, 1896, xxix., 666; 1897, xxx., 2530), so that their constitution as chemically individual substances cannot be doubted. They are not to be regarded therefore as "eminently unstable" and "impure," as Armstrong and Robertson assert. As a matter of fact, some of the *syn*-derivatives are so stable as to be only convertible with difficulty into the more stable isomeric *anti*-form.

The undoubted existence of these two classes of compounds (the representatives of the stereo-isomeric azo-compounds), which Armstrong and Robertson do not admit, provides therefore the strongest proof for my stereochemical theory of the diazo-derivatives, a theory supported by a large mass of experimental evidence, in connection with which the theoretical signification has always been carefully pointed out. The reflection by Armstrong and Robertson on the accuracy of this work is altogether unwarranted, and with a thorough knowledge of the subject, it is impossible for me to understand how such assertions could be made.

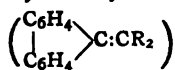
I am forced to conclude that they have not thoroughly informed themselves in respect to my experimental investigations. Above all, I have to deplore that the numerous exact analytical results already published should thus be brought into discredit, and the stereo-chemistry of the diazo-derivatives founded on them regarded as "unnecessary in fact"; to be replaced by a view with which the facts, indeed the principle itself, stand in direct contradiction.

In reply to the statement that "I am opposed in principle to conclusions based on optical evidence" (*Ber.*, 1899, xxxii., 3149), it is only necessary for me to say that such conclusions in regard to constitution are not warranted from a mere consideration of the optical properties, more especially when these stand in contradiction to the general chemical behaviour of the substance.

It is certainly a very great surprise to me that such a statement should be brought forward, for I have always regarded the physico-chemical behaviour of the substance as of very great importance, and especially in relation to the colour of substances as denoting their constitution. Thus, some eighteen years ago, in conjunction with Hermann (*Ber.*, 1887, xx., 2801), I was one of the first to draw attention to the relation between colour and constitution in the case of desmotropic substances, and recently, as a result of my researches on pseudo-acids, I have been able to show experimentally that the appearance of colour in the formation of coloured alkali salts from hydrogen compounds is due to an intramolecular change taking place in the position of a hydrogen atom. I intend publishing

shortly an account of several researches dealing with the relation of colour to constitution, and in particular establishing the quinonoid structure for nitrophenols, a theory first put forward by Armstrong on very slender experimental evidence, and certainly not accepted by a large number of chemists at the present time.

Summarising, it is my firm conviction that the colour of substances is one of the most important criteria in the characterisation of their constitution, but at the same time it is also one of the most delicate and subtle. Unfortunately, it is in so very many cases quite impossible to explain the origin of the colour, or to account for the remarkable phenomena by structural formulæ. It is only necessary to recall the existence of the coloured fulvene, of the coloured diphenylene-ethylene derivatives—



on the one hand, and the colourless polyacetylene on the other; of the coloured derivatives of diethoxynaphthostilbene, dibenzoylethylene, and benzaldehydobenzoine compared with their colourless isomeric modifications.

In short, as pertaining in particular to the azo- and diazo-derivatives considered in the light of their chemical and physical properties, there exist both coloured and colourless azo- and diazo-compounds, the cause of which colour is unknown, and which, although representable by Baeyer's valency formulæ ($\text{Ph}\cdot\text{N}:\text{N}\cdot\text{R}$ colourless, $\text{Ph}\cdot\text{N}=\text{N}\cdot\text{R}$ coloured), remain still unexplained by any rational structural formulæ. Above all it should not be overlooked that a sharp line of demarcation between coloured and colourless substances does not exist either theoretically or practically; for the same complex appears in an intensely coloured, a pale coloured, or a colourless substance, according to the nature of the groups associated with it. Thus, in the case of the aromatic azo-complex $\text{Ph}\cdot\text{N}:\text{N}$, when this is attached to nitrogen the colour-intensity of the products is less than when it is attached to carbon (thus, $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ possesses a lighter yellow colour than $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{CN}$ or $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{Ph}$). It is therefore comprehensible that when the same complex is attached to oxygen (as in the diazotates $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OR}$) we have a colourless substance formed, more especially as the diazo-compounds containing the group $\text{RO}\cdot\text{N}:\text{N}\cdot\text{OR}$ (for example, hyponitrous acid, salts, and esters) are also colourless.

We have accordingly in the following series of colour intensities:—

$\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OR}$	$\text{Ph}\cdot\text{N}:\text{N}\cdot\text{NHR}$	$\text{Ph}\cdot\text{N}:\text{N}\cdot\text{CN}$
Colourless.	Pale coloured.	Intensely coloured.

a collection of facts which we cannot explain or represent satisfactorily by structural formulæ.

The change of condition from the coloured to the colourless state in azo-compounds is bound up with, but not, however, altogether dependent on, the known structural and stereochemical isomerism of the diazo-derivative; that is, presence or absence of colour is not definitely decided by such isomerism; for whilst both classes of the stereo-isomeric diazotates are colourless, both those of the stereo-isomeric diazosulphonates and diazocyanides are coloured. Since Armstrong and Robertson's views and formulæ are quite untenable, the older structural and stereochemical formulæ indicate now, as before, the best and most accurate representation of the facts concerning the diazo-compounds.

212. "Note on the Incandescent Mantle as a Catalyst and its Application to Gas Analysis." By JOHN ERNEST MASON and JOHN WILSON.

The method described by Lewes (CHEMICAL NEWS, 1905, xci., 61) for demonstrating the incandescence of the ordinary gas mantle in a cold mixture of coal-gas and air may also be employed with a mixture of ammonia vapour and air. The authors described a modification for showing the incandescence of the mantle in an unburnt mixture of

alcohol vapour and air. Although less effective, the mantle may be used as a substitute for platinised asbestos in the ordinary lecture experiments for preparing formaldehyde from methyl alcohol vapour and air, and sulphur trioxide from sulphur dioxide and oxygen.

Fragments of mantle in a hard glass or preferably quartz tube may be used in place of palladium or palladium-asbestos, for the estimation of hydrogen and carbon monoxide in gas analysis by combustion with excess of air or oxygen. Methane and mixtures of methane and hydrogen may be estimated similarly by passing these gases mixed with excess of oxygen over fragments of mantle heated in a quartz tube, and measuring the contraction after combustion and subsequent treatment with caustic potash solution. The results agree well with those obtained by the customary explosion methods. Good results may also be obtained by passing the gases mixed with oxygen over asbestos heated in a small quartz tube. Hydrogen, and less readily methane, may be estimated by passing the gas mixed with oxygen through narrow tubes of heated Jena glass alone.

213. "The Influence of certain Amphoteric Electrolytes on Amyolytic Action." By JOHN SIMPSON FORD and JOHN MONTEATH GUTHRIE.

An investigation of the influence of asparagine, glycine, and α -alanine on amyolytic action has led to the following conclusions:—

1. Asparagine and the amino-acids mentioned have no specific influence in augmenting the action of amylase; the apparent augmentation of action sometimes obtained by the addition of these amphoteric substances (or of feeble acids) is due to their neutralising alkaline (or other) impurity in the starch or enzyme solution.

2. Normal amyolytic action takes place in neutral solution. In the plant substance, this neutrality is brought about by equilibrium between the basic and acid products present.

3. Until the conditions influencing the action of enzymes are more fully established, it is inadvisable to formulate mathematical laws as to the kinetics of enzymic hydrolyses.

4. Purified soluble starch has the properties of an extremely feeble acid; it is capable of yielding negative ions under the influence of strongly positive ones.

214. "The Estimation of Picric Acid Additive Compounds." By FRANK STURDY SINNATT.

The method of Knecht and Hibbert (*Ber.*, 1903, xxxvi., 1549) for the estimation of picric acid by means of titanous chloride has been found to be applicable to other picrates, and also to picric acid additive compounds.

Twenty-five c.c. of a solution of 0.200 grm. of naphthalene picrate in 250 c.c. of alcohol were titrated with titanous chloride, and gave 99.49 per cent of naphthalene picrate. Pyridine and strychnine picrates yielded 100.19 and 99.69 per cent respectively.

In many cases it is convenient to dissolve the picrate in hydrochloric acid. The method has been applied to the estimation of naphthalene in coal-gas; the naphthalene picrate is separated by the usual process (Colman and Smith, *Journ. Soc. Chem. Ind.*, 1900, xix., 128), washed, dissolved in a small volume of alcohol, and titrated with titanous chloride. If a standard solution of picric acid is used in the wash-bottles, the filtrate and washings may also be titrated. The results compare with those obtained by Colman and Smith's method. The estimation of naphthalene and the applications of the titanous chloride process to other picric acid additive compounds are being continued, and the results will be embodied in a further communication.

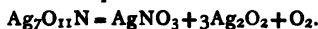
215. "Silver Dioxide and Silver Peroxynitrate." By EDWIN ROY WATSON.

A black crystalline product, obtained at the anode during the electrolysis of an aqueous silver nitrate solution, was considered by Ritter to be silver dioxide, Ag_2O_2 (*Gehlen's Neues Journ.*, 1804, iii., 561). Later investigations showed

that it could not be regarded as silver dioxide, and a variety of conflicting formulæ have been proposed.

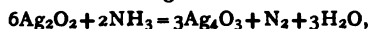
The author has electrolysed aqueous silver nitrate with different current strengths and densities, and with solutions of varying concentrations, and has analysed the product formed at the anode in order to see whether this should be regarded as a definite chemical compound or as a mixture, the composition of which varies with different conditions. It was concluded that the product was a definite chemical compound, and that its composition was correctly represented by Sûlc's empirical formula $\text{Ag}_7\text{O}_{11}\text{N}$. The substance is easily decomposed by heat or when left in contact with water or organic matter, such as filter-paper, and to this cause must be attributed the divergent results of the earlier investigators.

This compound, silver peroxynitrate, as it has been termed by Tanatar, on boiling with water decomposes in accordance with the equation—



Silver dioxide is a greyish black powder (sp. gr. 7.44), which may be heated to 100° without decomposition. At higher temperatures it gently decomposes into its elements. It dissolves in hot dilute sulphuric acid in accordance with the equation $2\text{Ag}_2\text{O}_2 + \text{H}_2\text{SO}_4 = 2\text{Ag}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{O}_2$.

Its behaviour with ammonia is noteworthy, and may be represented in the following manner:—



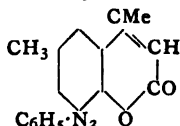
so that the compound in solution must be regarded as a polyvalent silver compound, probably $\text{mAg}_4\text{O}_3 \cdot \text{nNH}_3$.

The dioxide of silver and silver peroxynitrate both dissolve in cold concentrated nitric acid with the production of an intensely brown solution, the colour of which gradually fades even at the ordinary temperature, and much more rapidly on warming. The rate of decomposition of the compound is proportional to its concentration in the solution, a fact which makes it impossible to give to the compound the simple formula $\text{Ag}(\text{NO}_3)_2$. The formulæ $\text{Ag}_4(\text{NO}_3)_8$ and $\text{Ag}_2(\text{NO}_4)_2$ are, however, possible.

216. "The Constitution of *o*-Hydroxyazo-compounds. Preparation of Benzeneazodimethylcoumarin." By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

The authors have hydrolysed the 4 : 6-dimethylcoumarin described by Pechmann and Cohen (*Ber.*, 1884, xvii., 2118), and have coupled the alkaline coumarinate so obtained with phenyldiazonium chloride and the three nitrophenyldiazonium salts.

The alkaline azocoumarinates so obtained are highly coloured, varying in shade from red to violet. On acidification, light coloured anhydrides of the type—



are precipitated.

This instantaneous dehydration indicates the existence of a ready-formed hydroxyl group, even in the *o*-hydroxyazo-series.

Benzeneazo-4 : 6-dimethylcoumarin melts at $199-200^\circ$; the *o*-, *m*-, and *p*-nitrobenzeneazo-4 : 6-dimethylcoumarins melt at $240-250^\circ$ (with decomposition), 212° and 229° respectively, these melting-points being corrected.

217. "Caro's Permonosulphuric Acid." By THOMAS SLATER PRICE.

Hitherto it has not been possible to decide between the formulæ H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_9$ for Caro's permonosulphuric acid. The decision could readily be made if a pure salt, for example, the potassium salt, could be obtained. The simplest method would be to heat a weighed quantity of the salt and determine the weight of potassium sulphate left; this weight would depend on whether the formula was KHSO_5 or $\text{K}_2\text{S}_2\text{O}_9$.

The author has not yet succeeded in preparing the pure potassium salt, but a mixture has been obtained containing the potassium salts of sulphuric, permonosulphuric, and perdisulphuric acids, and also potassium hydrogen sulphate. It was found possible to determine the amounts of each of the constituents present, and thus calculate the weight of potassium sulphate which would be left on heating up a known weight of the mixture; this could then be compared with the actual weight found. The results obtained point to the formula H_2SO_5 as the correct one.

NOTICES OF BOOKS.

Qualitative Chemical Analysis, Organic and Inorganic. By F. MOLLWO PERKIN, Ph.D. Second Edition. London, New York, and Bombay: Longmans, Green, and Co. 1905.

As some time has elapsed since the first edition of this book was published, it may be worth while to explain shortly its plan, which presents some novel features. The author has skilfully dovetailed in theory with practice, so that the student is obliged to think what he is doing, and is prevented from falling into a mechanical habit of work. The usual group tests are given, together with full analytical tables and schemes of separation; but the discussion of the results and the excellent summaries—as, for instance, in the case of the separation of arsenic, antimony, and tin—are characteristic features which mark the book out as specially valuable for training the student in good mental habits. Organic chemistry is treated at greater length than is usual in books of this kind, and copious additions have been made to this part in the second edition, which also contains considerably more theory than the original. The discussions of theory are interspersed among the practical work, and not, as a rule, placed apart—a plan which has many obvious advantages to recommend it.

Elementary Practical Metallurgy: Iron and Steel. By PERCY LONGMUIR. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THIS work may be regarded as an elementary introduction to the study of the metallurgy of iron and steel which is intended specially for the beginner. The author has endeavoured to make the subject as attractive and interesting as possible, and lays most stress upon practical points of view, while the theory is neglected, except when it bears directly upon practice. The treatment is quite elementary, and seems to present no striking novelties in any direction, so much so that the reader is led to wonder whether the book will fulfil any special purpose, not satisfactorily provided for in some of the numerous other books which have been written having practically the same scope and resembling it in many respects. The insistence upon practical methods and practical results is a good feature of the book, and the beginner, using it as an introduction which does not pretend to go into details, may safely trust to the author's accuracy.

Food Preservatives; their Advantages and Proper Use. By R. G. ECCLES, M.D., Ph.D. With an Introduction by E. W. DUCKWALL, M.S. New York: D. van Nostrand Co. 1905.

THE vexed question of the toxic effects of preservatives in food is discussed at considerable length in this book, and the sub-title, "The Practical *versus* the Theoretical Side of the Pure Food Problem," gives some idea of its scope and object. An account is included of the various preservatives in common use, but we notice some omissions in the list. For instance, no mention is made of the compounds of fluorine, although the use of ammonium fluoride in beer is by no means uncommon. Rough

methods of detection are given, but no estimation processes, nor are any notes on the sensitiveness of the various tests added. As regards the author's arguments in favour of the free use of preservatives, both partisans and opponents of the theories put forward must recognise the futility of heated writing in any form, especially in a scientific work of this kind, and also of the introduction of personal matters, which, after all, only concern the *bond fides* and accuracy of two authors, the writer of this book and the professor whose statement he calls in question. The impartial critic, after reading such a book, cannot fail to be convinced that those who hold diametrically opposite views must be possessed of very strong arguments to call forth such vehement criticism. It is typical of the author's mind and method that he compares those who disagree with him as regards the labelling as "adulterated" foods which contain preservatives, to the people who hunted down heretics in the olden times, and whose rancour was caused by the dislike of change in mental food, while the same quality of the modern heresy persecutors is caused by the dislike of the introduction of changes in man's physical food.

Modern Theory of Physical Phenomena. By AUGUSTO RIGHI. Authorised Translation by AUGUSTUS TROWBRIDGE. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1904.

THE Italian version of this work was much read, and it seems probable that the translation will be equally appreciated by a certain class of readers in England. Professor Righi's style is admirably suited for the production of such a work as this, for he has to a high degree the power of illustrating and explaining vividly and making the elementary treatment of a subject very readable and interesting. For the benefit of those whose scientific knowledge is slight he discusses the nature of electrons, cathode rays and ions, the phenomena of radio-activity, and the constitution of matter, explaining very clearly the chief features of the theory which has been built up on the basis of the observed facts. It requires no small skill to produce such an excellent elementary work, and Professor Righi is greatly to be congratulated on his interesting little book.

Introduction to the Study of Organic Chemistry. Second Edition. By JOHN WADE, D.Sc. (Lond.). London: Swan, Sonnenschein, and Co., Ltd. 1905.

THE plan of this book is thoroughly sound and the working out no less satisfactory. The author aims at inducing students to build the foundations of their knowledge of organic chemistry on facts which they have discovered experimentally, then deduce generalisations from these facts, and proceed to further experimental work suggested by these generalisations. Thus the student's knowledge should be thoroughly practical, and at the same time he would be training himself for research work and developing his logical faculties. Thus, as far as its aim is concerned, the book has very distinctive features, and we are not surprised to learn that the first edition was favourably received, for the details are admirably presented, and the treatment is decidedly original. Every care is taken to impress the essentials on the reader's mind, and the synoptical charts given at the end of nearly every chapter are admirably suited for this purpose. The number of these charts has been considerably increased in the new edition, and they are now provided for practically every series of important transformations and syntheses. Briefly, the plan is worked out as follows:—The first part deals with typical compounds of simple constitution, the nature and properties of some of the important classes of organic compounds being investigated, and the conception of the organic radical introduced and thoroughly explained. The second section deals with synthesis and molecular structure, which subjects are afterwards further developed in Section IV. Sections III. and V. to XVII. treat systematically

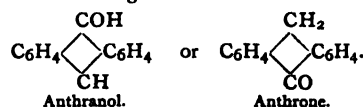
of the various classes of carbon compounds. Then follows one of the most useful parts of the book, that is the appendix of supplementary laboratory notes, which gives details of the preparation and purification of practically every compound which may advantageously be prepared by the student in the laboratory. This part has been much extended in the new edition, and now provides a complete course of practical organic chemistry, a short scheme of qualitative analysis having been added.

CHEMICAL NOTICES FROM FOREIGN SOURCES

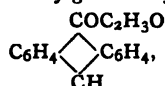
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 22, November 27, 1905.

Distillation of Copper.—Henri Moissan.—The author has shown by previous researches that refractory bodies no longer exist, and that while certain compounds are decomposed by simple raising of temperature, others are formed at high temperatures—such as carbides, silicides, and borides—decomposing, according to M. Violle, at a temperature approaching 3500°. In his notes of 1892–1893, the author has shown that all metals can be volatilised in the electric furnace, and he has continued his researches in order to classify the boiling-points of certain metals, hoping that the physicists will be able to determine accurately these temperatures. In 1859 by Despretz, and in 1882 by Siemens and Huntingdon, it was shown that small quantities of copper volatilised by the heat of the electric arc at atmospheric pressure. In 1905 Kraft and Bergfeld showed that copper boiled at 1600° in the cathodic vacuum. The author, by using his electric furnace and following the experiments of Kraft and Bergfeld, heated 300 grms. of copper for five minutes in a current of 300 ampères under 110 volts. The metal melted, and after three minutes began to boil, the distillate being collected on a tube cooled by a rapid current of cold water. At the end of the experiment it was found that 50 grms. had been distilled. A second experiment gave 160 grms. in six minutes, and a third 233 grms. in eight minutes. The author describes in detail the appearance of the condensed product, finding it contains 99.76 per cent of copper, which behaves chemically exactly like copper filings. The deposit on a cylindrical receiver, placed over the perforated lid of the furnace, consisted of oxide of copper, quicklime, and black globules; consequently the copper vapour in contact with the air had burnt to little globules of black oxide, some of which enclosed a nucleus of red metal. The metal in the crucible contained small quantities of iron, lime, and aluminium, derived from the impurities in the electrodes, but far more important than this was the presence of graphite. This graphite—sometimes amorphous, sometimes crystalline—separated by nitric acid, washed, and dried, had a density of 2.12. By using a current of 800 ampères under 110 volts, and taking a crucible which can hold 8 to 10 k.grms. of copper, the author states that several kilograms may be distilled in a few minutes. He concludes—(1) That copper is readily distilled by the electric furnace; (2) that when the vapour condenses on a cold surface, a filament deposit of copper is obtained having all the properties of ordinary copper; (3) that at its boiling-point copper dissolves graphite, which separates out in more or less crystalline form on cooling.

Benzylidene Derivatives of Anthrone or Anthranol.—A. Haller and M. Padova.—Liebermann, in 1882 and 1887, isolated the compound $C_{14}H_{10}O$ from among the products of reduction of anthraquinone, and gave to it one or other of the following formulæ:—



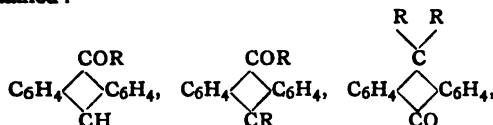
Since this compound readily gives acetylanthranol,—



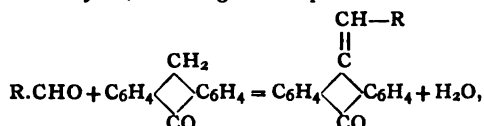
he decided in favour of the first formula. Later, Goldmann

showed that, with chlorine, the chloride, $\text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4 \text{---} \text{CO}$

is formed and (in another work) that, on treatment with potash and alcoholic iodides, the three following are obtained:—



the last evidently being a dialcylol derivative of anthrone, while the first two revert to anthranol. According to circumstances, then, the compound $\text{C}_{14}\text{H}_{10}\text{O}$ behaves either as a hydroxy-anthranol or a methylene derivative (anthrone), and in support of the latter is the formation of non-saturated compounds on condensation with aldehydes, according to the equation—



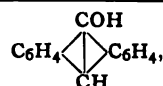
as in the case of benzylidene anthrone or dehydrobenzyl-oxanthranol, prepared at first by Levi, and later by C. Bach, by the dehydration of benzylloxanthranol obtained by acting on anthraquinone by benzyl bromide in the presence of potash and powdered zinc. The authors have succeeded in preparing this benzylloxanthranol from anthraquinone and the organo-magnesium compounds according to the method of Grignard, and also by using benzyl-magnesium chloride instead of the magnesium compounds of brominated benzene or toluene. With sulphuric acid it loses water and yields the benzylideneanthrone. *Condensation of Benzoic, Anisic, and m-Nitrobenzoic Aldehydes with Anthrone.*—This is effected with the help of piperidine, the solvent being anhydrous pyridine. 1. Benzylideneanthrone (dehydrobenzylloxanthranol) was prepared by the authors by heating for six hours a mixture of anthranol (prepared by the method of Liebermann and Gimbel), benzoic aldehyde, dry pyridine, and piperidine. Yellow needles were obtained, melting at 126–127°, soluble in alcohol, chloroform, and benzene, and insoluble in ligroin, and giving the composition of benzylideneanthrone; 36 per cent of the theoretical yield being obtained. 2. Anisylidene, or $\text{p-C=CHC}_6\text{H}_4\text{OCH}_3$

methoxybenzylideneanthrone, $\text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4 \text{---} \text{CO}$

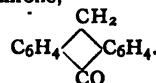
was prepared as the preceding. Crystallising from alcohol or acetic acid, yellow needles were obtained melting at 140.5–141.5°, and less soluble than the preceding in alcohol, acetic acid, acetic ether, chloroform, and benzene, and insoluble in ligroin. 3. *m*-Nitrobenzylideneanthrone, $\text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4 \text{---} \text{CO}$

, was prepared under the same con-

ditions and crystallising from acetic acid, and then benzene; it melted between 165.5° and 166.5°. Chloroform, benzene, acetic acid, and warm pyridine dissolved it easily, but it was only slightly soluble in methyl and ethyl alcohols, and not at all in ligroin and petroleum ether. The authors conclude that $\text{C}_{14}\text{H}_{10}\text{O}$ is a tautomeric compound, for it behaves, under the above conditions, not as anthranol,—



but as its isomer, anthrone,—



The authors intend to extend their investigations towards other anthranols.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xxxviii., No. 15, 1905.

Electrical Preparation of Colloidal Solutions of Selenium and Sulphur.—Frich Müller and Romuald Nowakowski.—Already noticed.

Compounds of Chromium containing Pentavalent Chromium.—R. F. Weinland and Walter Fridrich.—If a solution of chromic acid is allowed to stand for some time in hydrochloric acid saturated at 0° some chlorine is evolved, and the liquid becomes dark reddish brown; when a solution of pyridine or quinoline in strong hydrochloric acid is added, after a short time brown-red glistening flakes are obtained. Analysis shows that they contain one atom of chromium to four atoms of chlorine and one molecule of pyridine (or quinoline), and by iodometric determination of the oxidation products of the chromium the authors found that two-thirds of the chromium in the compound is hexavalent and one-third trivalent. This corresponds to an oxide, $4\text{Cr}^{\text{VI}}\text{O}_3 + \text{Cr}_2^{\text{III}}\text{O}_3$ or $\text{Cr}_2^{\text{V}}\text{O}_5$, and the simplest assumption is that the compounds repre-

sent salts of a meta acid, $\text{Cr}^{\text{V}}\text{O}_3\text{H}$ or $\text{Cr}^{\text{V}}\text{O}_3\text{H}$, in which two atoms of oxygen are replaced by four atoms of chlorine. This assumption was confirmed by the determination of the molecular weight of the pyridine salt cryoscopically in glacial acetic acid; this gives a molecular weight corresponding to the formula $\text{CrCl}_4(\text{OH})\text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}$. As regards the stability of the compounds, the pyridine salt can be kept over sulphuric acid, but gradually decomposes in the air, turning yellow. The quinoline salt is much less stable, and rapidly becomes orange-red, and finally yellow in the air. If after the compound has become yellow, fuming sulphuric acid is added to it, it again becomes brown-red. Chlorine is evolved when the compounds stand in air, so that a part of the chromium must be reduced to the trivalent state. In strong hydrochloric and in glacial acetic acid the salts dissolve without decomposition. The aqueous solution is yellow, and gives with ammonia a precipitate of chromium hydroxide, and with lead acetate a precipitate of lead chromate. Thus we must assume that water splits the acid of pentavalent chromium into compounds of hexa- and trivalent chromium, the decomposition being exactly analogous to that produced by water in the case of manganic acid, when permanganic acid and manganese dioxide are formed.

Sodium Hydrosulphite.—A. Binz and W. Sondag.—Sodium hydrosulphite reacts with sodium thiosulphate, forming sodium sulphide. To ascertain the course of the reaction, the different forms in which the sulphur was present were determined quantitatively by the following experiments:—A weighed quantity of the powdered hydrosulphite was titrated with standard potassium ferricyanide in a current of carbon dioxide. This titration proved the presence of 80.2 per cent $\text{Na}_2\text{S}_2\text{O}_4$. Then from another weighed quantity the sulphur dioxide was removed by boiling with hydrochloric acid and carbon dioxide. The liquid was filtered from sulphur, and in the filtrate the sulphate sulphur was determined by precipitation as barium sulphate; this amounted to 0.93 per cent. A weighed quantity of the hydrosulphite was converted into tetra-thionate, which, when boiled with hydrochloric acid and pure aluminium foil in a current of carbon dioxide, gave an

amount of sulphuretted hydrogen corresponding to 0.67 per cent thiosulphate sulphur. The sulphite sulphur amounted to 4.60 per cent, and was determined by shaking the substance with sodium hydroxide solution (1.7 per cent) in air, decomposing the thiosulphate with mercuric chloride, and driving off the sulphurous acid into $\frac{1}{10}$ N iodine solution. A portion of the hydrosulphite powder was then warmed to 57–62° for five hours in absence of air with sodium thiosulphate and caustic soda. The amounts of sulphur in the form of hydrosulphite, sulphide, sulphite, thiosulphate, and sulphate were then determined, and these were found to agree with the following equation, which represents the reaction between hydrosulphite and thiosulphate:—



Determination of Nitric and Nitrous Acids.—Jacob Meisenheimer and Friedrich Heim.—The authors have devised a method by which nitrous acid can be determined conveniently, quickly, and accurately, and which is well suited for the estimation of nitric and nitrous acids in presence of one another. The separation of the two acids rests upon the already known reactions represented by the following equations:—(1) $\text{HNO}_2 + \text{HI} = \text{NO} + \text{I} + \text{H}_2\text{O}$, (2) $\text{HNO}_3 + 3\text{FeCl}_2 + 3\text{HCl} = \text{NO} + 3\text{FeCl}_3 + 2\text{H}_2\text{O}$. The faintly alkaline solution of the substance (0.1 to 0.2 grm. nitrite) is placed in a round flask closed by a three-holed rubber cork. Through the holes of the cork pass—(1) a tube bent twice at an acute angle, the free end being narrowed to a point which dips into a trough filled with 12 per cent caustic soda; (2) a tube from a Kipp's apparatus generating carbon dioxide which is washed with potassium carbonate solution. This tube reaches nearly to the bottom of the round flask; (3) a separating funnel, which before the experiment is filled up to the cock with pure water. All the air is first expelled by passing a current of carbon dioxide for ten minutes, after which over the end of the bent tube a eudiometer tube filled with 12 per cent caustic soda is placed. Then 10 to 15 c.c. of a 5 per cent potassium iodide solution are introduced into the flask through the separating funnel, and an equal amount of dilute hydrochloric acid. The nitric oxide begins to be evolved at once, and the reaction is hastened first by gentle warming and then by heating until a state of incipient ebullition is reached, a current of carbon dioxide being simultaneously passed through the apparatus so that the last traces of nitric oxide may be expelled. As soon as the volume of gas obtained no longer increases, the eudiometer is removed, well shaken, and transferred to a high cylinder with water, and left for ten minutes. If the nitric acid is to be determined in the residue, a fresh eudiometer filled with caustic soda is brought over the bent tube, and by means of the separating funnel 10 to 20 c.c. of a concentrated strongly acid solution of ferrous chloride in hydrochloric acid is introduced, and the experiment is then concluded as in Spiegel's modification of Schulze and Tiemann's method (*Berichte*, 1890, xxiii., 1361). The advantages of this method are—(1) it takes very little time—at the most an hour and a-half from beginning to end, if the apparatus is prepared beforehand—(2) the determination of both acids is performed on the same quantity of substance; and (3) both acids are determined directly, thus avoiding errors of indirect methods.

Modifications of Antimony.—Alfred Stock and Werner Siebert.—Like arsenic, antimony exists in three forms, yellow, black, and metallic-grey. The last is the most stable form and the only one existing in nature. Pure black antimony may be prepared by transforming the yellow form, by the action of oxygen or air on liquid antimony hydride at temperatures above -90°, and by rapid cooling of the vapours of ordinary antimony. This last operation may be performed in the apparatus devised by the authors for the conversion of black arsenic into the yellow modification (*Berichte*, 1904, xxxvii., 4572). The sublimation of the antimony must be effected at the lowest possible temperature, otherwise a grey instead of a black sublimate is obtained. For the second method of preparation of black

antimony, small bubbles of oxygen are introduced into liquid antimony hydride at about -40°. After evaporating off the antimony hydride, the fine velvety black powder is freed from oxide by treating it with hydrochloric acid, washed with alcohol and ether, and dried *in vacuo*. The third method of formation consists in warming the yellow form above -90°, or exposing it to the action of light at lower temperatures; it is of no practical importance. The black antimony thus obtained seems to be always amorphous, no crystallisation ever having been observed. If ordinary antimony is heated in an exhausted glass tube, at first a thin mirror of the black variety forms at some distance from the heated part, and soon, between this and the ordinary antimony, a metallic-grey deposit is produced. This shows that black antimony is more easily volatilised than metallic antimony. The density of the black variety is 5.3. It is chemically more active than the grey variety; it oxidises in air at the ordinary temperature, and when finely divided antimony, prepared from oxygen and liquid antimony hydride, is left at the ordinary temperature in contact with air it often ignites. If when it is being prepared the oxygen is allowed to act upon it too long a grey layer of oxide is formed on it; this may be removed by washing with hydrochloric acid. Black antimony, when warmed in absence of air, yields the metallic modification, an alteration taking place in appearance and density. The transformation takes place rapidly at 400°, and slowly on boiling with water. The black modification appears to be labile at ordinary temperatures, and the metallic form is stable. Antimony, like arsenic, is monotropic. The three elements, antimony, arsenic, and phosphorus, exhibit the interesting phenomenon that at the ordinary temperature the metallic form is stable in the case of the first, the black amorphous variety in the case of the second, and the yellow form (in absence of air) in the case of the third. When antimony chloride is reduced with aluminium, a black-looking metal is obtained; but in this and other cases it appears that a mixture of black and metallic antimony is formed. The yellow variety has been prepared by leading oxygen into liquid antimony hydride at -90°. On warming the yellow substance pure black antimony is formed. The yellow modification retains a small quantity of antimony hydride mechanically. When solutions of chlorine and antimony hydride react together in liquid ethane at -100°, pure yellow antimony separates out. After filtering and washing with pure liquid ethane (in a red light at -100°) the yellow antimony was dried at the same temperature in the vacuum of the mercury air-pump. It was found to be not perfectly pure, but on warming yielded small quantities of a gas. Yellow antimony is even more unstable than yellow arsenic. Above -90° it soon becomes black in the dark, and the same change occurs at a lower temperature in sunlight. When yellow antimony is warmed with carbon disulphide the liquid turns yellow, although this is not due to the solution of the antimony, as has been supposed, but to the conversion of the yellow into the black variety. A solution of yellow arsenic in carbon disulphide is quite colourless, but begins to turn yellow on standing, and yellow antimony behaves exactly similarly, the yellow liquid being not a true solution, but containing insoluble antimony in the colloidal state. It becomes colourless on filtering. The solubility of yellow antimony in carbon disulphide is very small at low temperatures, and only becomes appreciable at temperatures at which the resulting solution is no longer stable. "Explosive" antimony has been shown by Cohen to contain a modification of antimony which he calls "a-antimony," and the explosion is due to the transformation of the *a* into the ordinary variety. Probably "e-antimony" is identical with black antimony; to settle the question of its nature the heat of formation of grey antimony from the black variety must be determined.

MEETINGS FOR THE WEEK.

TUE.-DAY, JAN. 2 } Royal Institution, 3. (Christmas Lectures,
THURSDAY, " 4 } adapted to a Juvenile Auditory). "Astronomy,"
SATURDAY, " 6 } by Prof. Herbert Hal Turner, D.Sc., F.R.S.

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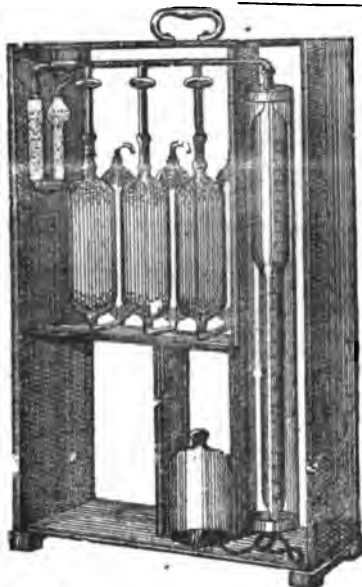
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